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THE PHYSICAL REVIEW

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THE

PHYSICAL REVIEW

EXTREME ULTRA-VIOLET SPECTRA

By R. A. Millikan and I. S. Bowen

Abstract

Extreme ultra-violet spectra, to 136 A, of twenty light elements, H to Cu.—Using the vacuum apparatus and explosive spark previously described, many plates have been made with a great variety of electrodes. By measuring and comparing thirty of these, over 800 lines between 136 A and 1862 A have been identified as belonging to one or other of the twenty elements studied. For H(1) only two lines, members of the Lyman series, were found; for He(2), and Li(3) none, though carefully looked for; for Be(4) one doubtful weak line; for Na(11) one strong line λ372.3 and one doubtful one λ376.6; for the other elements B(5), C(6), N(7), O(8), F(9), Mg(12), Al(13), Si(14), P(15), S(16), Cl(17), K(19), Ca(20), Cr(24) and Cu(29) from 9 to 160 lines each, all given in Tables. The strongest lines for each of the light elements are *L series lines* and form a progression like Moseley's for x-ray lines: Li (red), Be 3131.19, B 2066.2, C 1335.0, N 1085.2, O 834.0, F 656.4, Na 372.3, Mg 231.6, Al 162.4. These are mainly doublets, the separation increasing regularly with atomic number. *M spectra* also extend to shorter wave-lengths the higher the atomic number, reaching about 155 A for Cu, but on account of the complexity of the spectra only a few lines have been identified. *Other series lines* identified are: 2 diffuse series lines and 2 sharp series lines due to Mg^+ or Mg(II), 5 lines due to Al^+ and 9 due to Al^{++} or Al(III), 11 lines due to Si(IV) and probably the first terms of the principal series and of the diffuse series of P(V). *Interpretation in terms of Bohr theory.* By use of the Kossel equation in connection with available data it is shown that for Na, 372.3 A corresponds to an electron jump from the M shell to L(I); for Mg, 320.9, and 323.2 and 231.6 correspond to M(I)→L(II), M(I)→L(III) and M(III)→L(I); for Al, 162.4, 200.0, 230.8, 186.9 may correspond to jumps from shell 3 to the L shell; for Ca, 655.9 and 669.6 correspond to jumps N(I)→M(II) and N(I)→M(III). These interpretations give values of *constants of the L and M levels of the atoms as follows:* For Na, L(I), ν/R=2.826; for Mg, L(I) 4.298, L(II) 3.402, L(III) 3.381; for Al, L(I) 6.045, L(II) L(III) 5.008. The square roots of these values are linear functions of the atomic number. For Ca M(II), ν/R=1.839, M(III) 1.810. From the difference L(II)−L(III) for Mg, the *screening constant* comes out 3.1; from the difference M(III)−M(II) for Ca, the constant is 7. These results are all in good agreement with other data.

Ionization produced by explosive spark in vacuum.—The strongest spectrum lines are generally emitted by stripped atoms, that is atoms with no valence electrons left, Na(I), Mg(II), Al(III), Si(IV), P(V), etc.

A PRELIMINARY report has been made by one of us[1] upon the most conspicuous characteristics of the extreme ultra-violet spectra of the light elements from hydrogen up to aluminum (atomic numbers 1 to 13) as revealed by the work which pushed down to 136 A the limits of the region of wave-lengths explored by grating methods.

Since that report was made a very prolonged and detailed study and comparison of a large number of plates taken with many different electrodes has been made. This study has involved a double measurement by the second of us of not less than 5000 lines and the comparison by both of us of the spectra found on 30 different plates taken with different electrodes for the sake of deciding what lines belong to each particular element. It is the results of that study which are presented herewith.

The apparatus and methods have been sufficiently described in preceding articles. Since our main object thus far has been the location of as many new lines as possible, we have, of course, sacrificed resolution to intensity, not using in general more than a fiftieth of our theoretical resolving power. For some of the studies in which we are now engaged we are using higher resolution.

As indicated in the preliminary report the key to the identification of lines was first found in the discovery that between 1000 A and 330 A chemically pure magnesium and aluminum gave practically identical spectra while on the same plates the lines above 1300 A were all different and corresponded, the one to the well known spectrum of aluminum, the other to that of magnesium. This meant that the spectra on both plates below 1000 A was the nearly pure spectrum of the oxygen atom, since no other impurity of importance could be present. This identification of the oxygen lines was checked by the fact that the oxygen spectrum appeared practically complete with the use of all oxidizable electrodes, diminishing in intensity as the electrodes became less and less oxidizable and disappearing entirely with silver.

Having thus the oxygen spectrum and knowing in this way that there were practically no aluminum lines between 1300 A and 230 A we could obtain the correct spectrum of carbon in this region by subtracting from the observed carbon spectrum the oxygen and aluminum lines since these were the only probable impurities in carbon.

An extension of the foregoing method to a large number of plates and electrodes, many of which were compounds, obviously involves not only painstaking work but also a very considerable exercise of judgment especially in the case of the very weak lines. In the following tables where we have felt that there was little or no uncertainty we have classed

[1] Millikan, Nat. Acad. Sci. Proc. **7**, 289–294, Oct. 1921.

the line in question without comment under the element to which in our judgment it belongs. Where there was about equal probability that it belonged to either one of two elements, for example oxygen and sodium, we have listed it under both and have followed the figures representing the wave-length in each case by the symbol of the other element without other notation, thus:

Sodium	Oxygen
1345 O	1345 Na

To indicate a considerably greater probability that the line belongs to one rather than the other of the two elements in question it is also recorded under each but with a subscript 1 underneath the symbol of the element to which it is thought to belong and a subscript 2 underneath the symbol of the element to which it may, though with considerable improbability, belong. Thus in the following notation the weight is thrown on the oxygen and the probability that it belongs to sodium has been reduced.

Sodium	Oxygen
4567 O_1	4567 Na_2

In cases in which we feel much confidence that the line belongs to a given element but in which we wish to indicate a mere possibility that it belongs to another we list it under the first element alone but follow it by the symbol of the other element with the subscript 3. This notation is then our first stage of uncertainty.

Wave-lengths are given in I. A. units reduced to vacuum, the 1854.7 and 1862.7 aluminum lines being used as fundamental standards.

Wave-numbers are reciprocals of wave-length, the latter being carried in obtaining these reciprocals to two places of decimals although in the wave-length column but one decimal has been retained.

With this introduction we list the new lines which we have brought to light, something like a thousand in number, under their appropriate elements and follow each table with such comments as seem necessary.

HYDROGEN

The only hydrogen line which we get consistently on nearly all plates is the first member of the Lyman series at 1215.7 A. It is significant, however, that we have taken plates with certain electrodes, notably thallium, cadmium, and lead, without getting any trace of this line. This is excellent evidence that the hydrogen does not come from residual gases, from stopcock grease, or from the walls of the vessel, but rather from the electrodes themselves. It makes it probable too that it is not due to hydrogen gas or water vapor occluded in the electrodes since these

gases should be occluded in, or condensed upon, these three electrodes as much as upon others. It is significant also that although the line at 1215.7 A appears in intensity as high as 5, 6, and 7 on certain plates we have observed none of the other members of this series except the second, namely 1025.6 A and this has occurred in intensity 0 on but five out of thirty plates.

TABLE I

Hydrogen

Int.	λ	ν
0	1025.6	97507
4	1215.7	82254

TABLE II

Beryllium

Int.	λ	ν
3	1512.8	66102

HELIUM

No trace of any helium line of the ultra-violet series has ever been found in any of this work with metallic electrodes. We have looked carefully for the first member of the helium ultra-violet series beginning at 1640 A

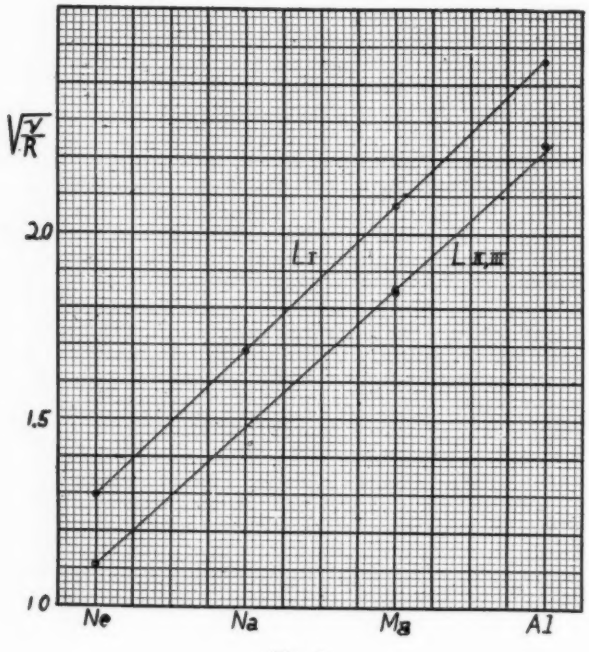

Fig. 1

but entirely without success. We have obtained with carbon electrodes a line at 585.7 A where Lyman finds a significant helium line, but in view of the entire absence of the afore-mentioned series have attributed this

line to carbon alone. Since in these experiments we are exploding the tips of our electrodes with the use of enormously more concentrated energies than have ever been used in exploding wires this means that the helium spectra which have been reported from exploding wires are due to impurities. Ten years ago one of us obtained what were believed to be

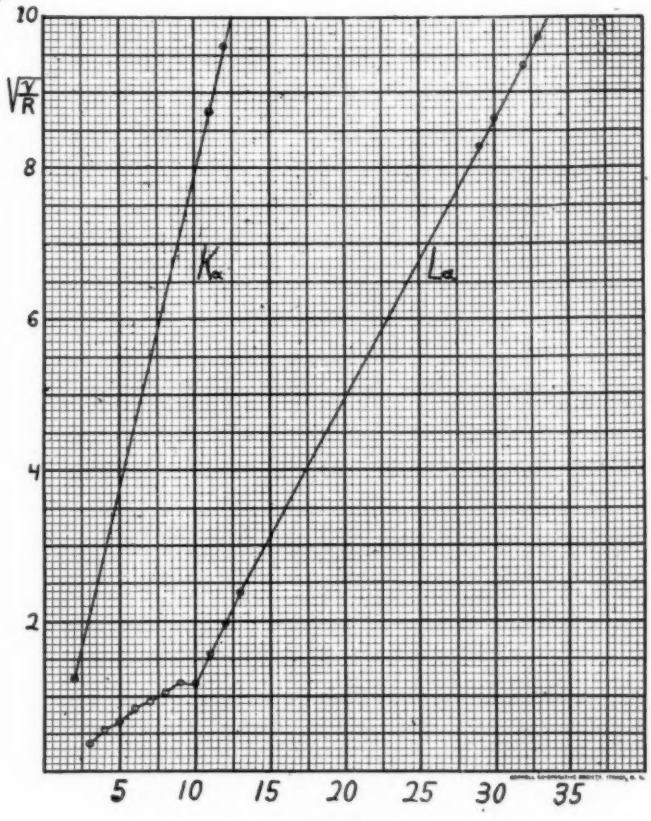

Fig. 2

helium lines in just this way from fresh electrode tips, but tired these lines out by repeated discharges, thus proving that they were due to impurities.

Lithium

The lithium spectrum was obtained from lithium metal held in pyrex tubes. As was to be expected the spectrum revealed the oxygen, hydrogen, and carbon lines. It showed also certain nitrogen lines of zero intensity and some weak silicon lines; but though the plate was an excellent one giving lines of the afore-mentioned elements from 370 A up

to 1700 A *there were in this whole region no lithium lines whatever*. This is striking proof that great gaps occur between the L and the K series in the optical region quite as well as in the x-ray field. The Kα line of lithium should occur at 240 A which is within the region accessible to our measurements, but want of the best of gratings when we were working on lithium has prevented us from getting it thus far. If, following the convention used in the preliminary paper we designate by Lα the strongest line of the L spectrum (spectrum due to jumps to orbits of total quantum number 2) the Lα line of lithium should be the head of its doublet series, i.e. the ordinary red line of lithium. This is the line plotted in Fig. 2.

Beryllium

The spectrum of beryllium was sought by using electrodes made by fusing a mixture of beryllium hydroxide $Be(OH)_2$ and borax $Na_2B_4O_7$ into tubes of carbon and later of aluminum. After the characteristic lines of sodium, boron, oxygen, aluminum or carbon had been obtained no additional strong lines that could be certainly ascribed to beryllium were found, but there is one weak line of as yet uncertain identity which is listed in Table II. However, new experiments with metallic beryllium electrodes are now being undertaken and the results will be reported later. According to the results thus far found by other observers the beryllium spectrum begins on the short wave length side at 2175 A and reaches its line of maximum strength at 3131.2 A. This is the Lα line plotted in Fig. 2.

Boron

The spectrum of the atom of boron was obtained by inserting metallic boron bound together with fused borax in the cores of carbon tubes. Further, borax was used as a flux in the taking of spectra on eight other plates, each of which gave opportunity to see whether these same lines always appeared and whether they all failed to appear when borax was absent. The only lines of those given in Table III about the identification of which there has ever been the slightest uncertainty are the lines at 758.5 A, 1230 A, and 1362.7 A. This last line had appeared in the spectrum obtained from the carbon electrodes and was at first thought to be due to carbon. But a comparison of all the plates taken when borax was used as a flux showed that it appeared in all of them, seven in number, in intensity from 3 to 8 while the most powerful carbon line at 1335.0 A of intensity 15 did not appear at all in some of them and very weakly in others, unless carbon was used as electrode material. This meant that the line in question was surely due to boron. Its appearance in the spectrum

obtained from carbon electrodes meant either that boron was present as an impurity in the carbon or else that carbon had a line of its own so close to 1362.7 A as to be indistinguishable from it with an instrument of the resolving power here used. To distinguish between these two alternatives we compare the boron and carbon spectra throughout and find that the strongest boron line, namely that at 1624.4 A of intensity 8, just appears in intensity 1 in carbon, while this line at 1362.7 A of intensity 5 in boron appears in intensity 5 in carbon, though the measured wave-length in carbon differs by the amount of .2 A, which is too small a difference to be certainly resolvable. We conclude, therefore, that though boron is a very faint impurity in our carbon electrodes there is in all probability a carbon line as well as a boron line in the immediate neighborhood of 1362.7 A and we record this line without comment under both boron and carbon. The foregoing is an illustration of the sort of analysis generally used in identifying lines. The final results for boron are found in Table III.

TABLE III

Boron

Int.	λ	ν		Int.	λ	
5	676.8	147748		5	1362.7	73383
0	731.2	136771		8	1624.4	61560
3	758.5	131832	O_2	0	1825.9	54767
2	882.3	113336		0	1829.8	54650
2	1081.7	92450		2	1842.9	54262
1	1230.0	81301	C_2			

CARBON

The carbon spectrum was obtained from electrodes made from gas carbon which showed as chief impurities, oxygen, nitrogen, silicon, hydrogen, and aluminum while traces of sodium, boron, and calcium also appeared. A comment upon the notation used in connection with the line at 538.4 A and some other lines of less prominence may here be made. This line has been inserted under both carbon and oxygen but in each table the line is followed by the symbol of the other of these two elements with a subscript 2. This means, when the carbon table, for example, is under observation, that this line is in all probability carbon though it is a bare possibility that it is due to an oxygen impurity, while when the oxygen table is under inspection the line is in all probability due to oxygen though there is a bare possibility that it is here due to a carbon impurity. These two at first sight contradictory notations signify that we have very good evidence that both oxygen and carbon have a line at about this wave-length. If we felt altogether certain of this result we should omit in both tables the O_2 and the C_2 but we leave them in to in-

dicate the possibility of an error in this conclusion. The actual evidence in this case is as follows: Line 538.4 A appears in intensity 7 with carbon electrodes when oxygen lines stronger than it do not appear there at all. This seems to show clearly that it is due to carbon. On the other hand it appears in intensity 4 with electrodes $NaF-Na_2B_4O_7-Al$ when only the three strongest carbon lines appear and they with intensity zero.

TABLE IV

Carbon

Int.	λ	ν		Int.	λ	ν	
0	360.5	277408		0	960.6	104106	
4	384.4	260166		0	966.6	103461	
4	386.4	258826		12	977.1	102343	
1	419.8	238197		10	1010.2	98990	
1	450.9	221769		1	1022.8	97775	
6	459.7	217552		11	1036.7	96461	
1	493.7	202569		8	1066.0	93812	
4	499.7	200140		3	1092.6	91522	
1	511.7	195419		3	1137.4	87920	
1	517.6	193192	O_2	4	1141.5	87608	
2	530.3	188590		15	1175.6	85062	
2	533.3	187501		3	1194.1	83743	Si_1
7	538.4	185742	O_2	2	1230.2	81289	
2	543.5	183993		7	1247.5	80158	
2	549.6	181953		5	1262.4	79213	
3	560.5	178399		5	1278.7	78204	
3	564.7	177085		2	1296.8	77112	
6	574.5	174052		1	1310.5	76307	
3	585.7	170745		2	1322.3	75626	
5	595.1	168045		7	1323.7	75544	
1	600.2	166606	O_1, K_2	4	1329.4	75222	
1	609.5	164061	O_1	15	1335.0	74909	
1	617.7	161883		1	1356.2	73737	
3	636.3	157149		5	1362.6	73391	
5	641.8	155802		1	1426.9	70082	
6	651.5	153483		1	1432.2	69822	
0	661.5	151167		2	1463.7	68320	
8	687.3	145491		1	1482.1	67473	
0	711.0	140645		0	1527.9	65448	
0	743.6	134486		0	1533.1	65226	
0	749.6	133403		4	1548.8	64566	
1	786.5	127141		3	1550.9	64481	
5	799.9	125016		5	1561.3	64048	
6	806.7	123957		0	1573.5	63552	
5	810.0	123464		1	1577.6	63388	
0	848.4	117876		0	1592.6	62792	Al, Na
5	858.5	116481		5	1657.6	60328	
1	884.8	113026		2	1752.3	57068	
10	904.1	110606		4	1760.7	56795	Al
1	936.4	106798		1	1827.3	54727	
4	945.6	105752		0	1832.8	54561	
0	954.4	104775					

This means that this line in the spectrum must be ascribed to oxygen rather than to carbon since the study of the 28 other plates shows clearly that it cannot be due to sodium, fluorine, boron, or aluminum. These two lines of evidence taken together signify that in all probability there is a line in this region due to oxygen and another due to carbon.

The notation after the line at 600.2 A in carbon means that this line is probably the same as the unquestioned oxygen line at 599.5 A (see table 4) though the difference is a little more than the error of observation if both lines were sharply defined. The line at 600.2 A in Table II, however, is weak and hard to measure accurately so that we wish to leave open the possibility that there may be a faint carbon line close to the strong oxygen line at 599.5 A. The K_2 after the O_1 signifies that we wish to leave open the bare possibility that this line is due to potassium in which there is a strong line (see Table XV) of intensity 4 at 600.2 A. Since potassium is a very oxidizable element this line too may be due to oxygen. It will be noticed that the line at 1194.1 A is included in both the carbon and the silicon tables and that it is followed in the former by the symbol Si_1 and in the latter by C_2 thus indicating that it is probably due to silicon but possibly to carbon. The strong lines due to the 4 electron L-ring of carbon are all included between 360.5 A and 1335.0 A where the strongest carbon line is found (see Plate I). In harmony with the foregoing convention this is plotted in Fig. 2 as the Lα of carbon.

NITROGEN

The chief characteristics of the nitrogen spectrum were predicted before they were obtained experimentally. The carbon spectrum had been found beginning on the short wave-length side at about 360 A, its lines gaining in intensity with increasing wave-length till they reached a powerful climax in the line at 1335 A, which had been taken in accordance with the foregoing convention as the Lα line of carbon. Similarly the oxygen spectrum had been found beginning at about 140 A and reaching an

TABLE V

Nitrogen

Int.	λ	ν	Int.	λ	ν
0	660.3	151458	4	916.3	109132
1	671.5	148925	6	991.0	100912
5	685.5	145875	7	1085.2	92152
1	747.0	133871	2	1134.8	88124
3	764.1	130873	0	1190.6	83989
2	772.3	129480	0	1242.2	80500
2	775.9	128878	0	1492.9	66984

unmistakable maximum of intensity in the powerful line at 834 A, the Lα line of oxygen. A general progression of spectra with atomic number toward higher and higher frequencies had been unmistakably observed, but no nitrogen lines in the extreme ultra-violet were known at all except the 1492.8 and 1494.8 lines reported by Lyman. It was clear from this progression that a strong Lα nitrogen line must exist between 834 A and 1335 A since the atomic number of nitrogen lay between that of carbon

and oxygen. Accordingly ammonium nitrate was fused into the cores of aluminum electrodes and the spectrum shown in Table V was at once obtained with its strong line at 1085.2 A (see Plate I). This spectrum was also checked by using sodium nitrite in carbon electrodes.

Oxygen

The oxygen spectrum is given in Table VI. The method of obtaining it has been already detailed. It will be noticed that all of the lines save one of wave-length above the very strong line at 834 A have a zero intensity while that one has an intensity of but 1. This is strikingly shown in

Table VI

Oxygen

Int.	λ	ν		Int.	λ	ν	
0	136.6	732332	Al	0	562.0	177949	
0	144.3	692809	Al	0	567.5	176199	Al
0	219.1	456413?	Al	0	580.6	172230	
0	221.5	451508?	Al	1	597.7	167314	
0	225.9	442693?	Al	5	599.5	166800	
0	233.8	427807		2	608.3	164398	
1	238.6	419041		3	610.1	163913	
0	260.7	383583		3	616.7	162161	
0	267.1	374420		4	625.2	159946	
0	272.4	367121		3	629.6	158823	
1D	279.7	357513		3	644.0	155272	
1	295.8	338043		0	656.7	152270	Al_2
2	303.7	329294		0	658.4	151879	Al_2
3	305.7	327129		0	673.0	148586	
1	321.5	311003		6	703.1	142225	
1	328.7	304210		5	718.5	139187	
0	345.7	289302		2	760.3	131536	
0	352.9	283366	Mg	0	764.7	130763	N_1
0	355.3	281444	Mg	0	774.3	129151	
0	359.4	278211		2	779.8	128246	
4	374.3	267180		3	787.4	126997	
0	379.6	263435		3	790.1	126561	
2	395.7	252691		1	796.4	125562	
1	430.0	232585		0	802.0	124694	Al_3
2	434.5	230129		8	834.0	119904	
0	481.1	207853		0	898.8	111264	
2	484.7	206322		0	921.1	108568	
5	507.8	196943		1	923.1	108328	
0	515.5	194005		0	1025.6	97507	H
0	518.2	192965	C_2	0	1031.4	96952	
4	525.7	190223		0D	1152.6	86760	
2	538.4	185729	C_2	0	1195.5	83646	Mg_3
0	540.7	184939		0	1338.5	74711	
5	554.2	180453		0	1343.5	74435	Al_2

Plate I. The oxygen spectrum shown on this plate does not, however, extend below about 500 A but in the so called aluminum spectrum shown in Plate II all of the strong lines below 400 A are due to oxygen.

Fluorine

The fluorine spectrum was obtained through the use of sodium fluoride in the cores of aluminum electrodes. It contains but two strong lines at

607 A and at 656.4 A, the latter of which is taken, according to the foregoing convention, as the Lα line of fluorine. This line unfortunately does

TABLE VII

Fluorine

Int.	λ	ν		Int.	λ	ν	
0	378.6	264152	?	1	571.4	175009	
0	411.3	243149		7	606.9	164772	
1	420.1	238027		5	656.4	152351	
0	441.7	226408		0	694.0	144092	
0	445.3	224548		0	954.9	104728	C
0D	458.0	218355	Si	0	984.4	101586	Cl_3
1	464.9	215109		0	989.3	101077	
0	472.2	211779		0	1049.6	95271	
1	490.3	203944		0	1133.5	88219	
0	497.6	200973		0	1143.7	87439	
0	547.2	182745		0	1151.8	86822	0
2	567.5	176224	O_2, Al_3				

not show distinctly in the reproduction in Plate I. Indeed each of the accompanying reproductions fails to reveal some lines which are distinct on the original negatives.

SODIUM

The sodium spectrum obtained from electrodes of pure sodium as well as from sodium fluoride in aluminum tubes shows in both plates only one unmistakable line in the whole region studied (300 A to 2000 A) namely that at 372.3 A. The line at 376.6 A also appears definitely on the plate taken with pure sodium electrodes as can be seen clearly from Plate II, though it does not appear on the plate taken with sodium fluoride electrodes. Deficiency of intensity may perhaps be the cause of its absence in this latter case. There can scarcely be any trace of a doubt that the line at 372.3 A is the line of greatest intensity in the L spectrum of sodium, for a line is definitely predicted by the Bohr theory at this wave-length.

TABLE VIII

Sodium

Int.	λ	ν	Int.	λ	ν
2	372.3	268637	1	376.6	265562

This prediction is obtained as follows: The single electron in the outmost or M shell of the normal sodium atom is in an energy level whose frequency value is represented by the convergence frequency of the principal series of sodium $\nu_M = 41449.0$ ($\lambda = 2412.63$). When an electron is removed from the L shell of sodium the foregoing M electron jumps into its place. The frequency value ν_L of the level to which it jumps is related to the frequency ν_e of the emitted line and ν_M by the Kossel equation

$$\nu_e = \nu_L - \nu_M \qquad (1)$$

λ 372.3 A corresponds to $\nu_e = 268640$. These values of ν_M and ν_e give $\nu_L = 310{,}090$, whence $\nu_L/R = 2.8258$, and $\sqrt{\nu_L/R} = 1.6810$. Now the

values of $\sqrt{\nu_L/R}$ for the L_{II} L_{III} levels of aluminum, magnesium, sodium, and neon are as follows: Al = 2.28[2]; Mg = 1.87[2]; Na = 1.49[3]; Ne = 1.11.[4]

The observed line at 372.3 A cannot then correspond to the jump to L_{II} or L_{III} and must therefore correspond to the jump to the only remaining L level, namely L_I and we are now for the first time enabled to fix the value of the L_I energy level[2] in sodium at the above value, $\nu/R = 2.8258$. That this is correct will be shown in the next section by comparing it with the L_I levels for both neon and magnesium.

Magnesium

Table IX shows that there are but three reasonably strong magnesium lines in the whole range of our plates (see Plate II) and the position of these lines at 231.6 A, 320.9 A, and 323.2 A shows that they must belong to the L spectrum of magnesium. The very weak lines at 353 A and 355 A are probably due to oxygen. The other four weak magnesium lines which are in the neighborhood of 1700 A belong, the first two to the second term of the diffuse series of ionized magnesium and the last two to the second term of the sharp series.[5]

The Bohr theory predicts all of our three observed magnesium lines in the L series as follows.

Table IX

Magnesium

Int.	λ	ν		Int.	λ	ν	
2	231.6	431760		0	1735.2	57630	*II*,* $3p_2-4d$†
5	320.9	311643		1	1737.9	57540	*II*, $3p_1-4d$
4	323.2	309377		0	1751.0	57110	*II*, $3p_2-5s$
0	352.9	283366	O	0	1753.7	57021	*II*, $3p_1-5s$
0	355.3	281444	O				

* II means the singly ionized atom, i.e., the atom with one electron entirely removed. III means the doubly ionized atom, i.e., two electrons entirely removed.

† The series notation used is that introduced by Bohr (Ann. d. Physik **71**, p. 286) and now adopted by Fowler and Paschen.

There are two electrons in the M shell of magnesium both in orbits of the form 3_1 (total quantum number 3, azimuthal quantum number 1).[2] The only possible jumps from these orbits are into the L_I L_{II} L_{III} orbits. The last two jumps should correspond to a doublet, the $l\eta$ doublet of Bohr's most recent notation, the jump to L_I should correspond to his single line β_4. Consider first the jumps into the L_{II} L_{III} orbits. These are from the M_I orbit according to Bohr and Coster. The frequency

[2] Bohr and Coster, Zeits. f. Phys. **12**, 344-352, 1923

[3] This value is interpolated from the two adjoining ones.

[4] Computed from Horton and Davies ionization potential 16.7 volts, Roy. Soc. Proc. **98**, 124-146, 1920

[5] Fowler, Series in Line Spectra

value of the 3(1,1) level is the convergence frequency of the principal series of magnesium singlets[6] for which $\nu = 61672.1$.[5] Applying then Eq. (1) to each of our observed lines λ 320.9 A ($\nu = 311640$) and λ 323.2 A ($\nu = 309380$) we obtain $\nu_{LII} = 373{,}310$; $\nu_{LIII} = 371{,}050$; whence $\nu_{LII}/R = 3.4019$, and $\nu_{LIII}/R = 3.3813$, $\sqrt{\nu_{LII}/R} = 1.8444$, $\sqrt{\nu_{LIII}/R} = 1.8388$.

Heretofore these levels have been obtained by computation from the K absorption edge and the Kα lines, and the experimental data have not been sufficiently exact to differentiate between these two near-by levels. Bohr and Coster give the average level as 3.5 and Sommerfeld as 3.46. Our L_{II} L_{III} levels, which should be correct to about 0.1 percent, are in quite as good agreement with the approximate values given by Bohr and Coster and by Sommerfeld as could be expected from the sort of precision obtainable from the use of the K series data.

Again, according to Sommerfeld's analysis, the frequency difference between the L_{II} L_{III} levels is given by the equation[7]

$$\Delta\nu_L = \Delta\nu_H (Z-s)^4 \qquad (2)$$

in which $\Delta\nu_H$ is the frequency separation of the hydrogen doublet the value of which is .365 cm^{-1}, and $(Z-s)$ is the effective nuclear charge. For the atoms of high atomic number Z, the value of s is 3.5. Inserting our observed separation $\Delta\nu_L = 2260$, and the value of Z, namely 12, and solving for s, the result is $s = 3.1$. This is fairly close to the observed "screening constant" for large Z's. But according to the Bohr theory of the interpenetration of the electrons from the M, N, etc., shells, the value of s should be somewhat less for atoms devoid of shells beyond the L shell. In other words for atoms near neon s may be expected to be somewhat smaller than 3.5 as it is here found to be. Indeed from the L doublet in neon as given by Grotian[8] and Eq. (2) the value of s for neon is found to be 3.2 or within the limits of our error exactly the same as we find it to be for magnesium. This is very beautiful proof that our observed magnesium lines at 320.9 A and 323.2 A are in fact the L doublet of magnesium (see Plate II).

Returning now to the very sharply defined singlet at 231.6 A. If Bohr's general scheme[5] were of universal applicability this would correspond to the β_4 line as already indicated, but Bohr himself shows that the 3(2,1) or M_{II} level does not exist, and that this sort of lack is common to all the substances having the alkali-earth type of spectrum.[6] The only M levels, not barred out here by the selection principle, which are actually revealed by the optical series in magnesium are those of fre-

[6] Bohr, Ann. der Phys. **71**, 281-288, 1923
[7] Sommerfeld, Atombau and Spectrallinien, pp. 607-618
[8] Grotian, Zeits. f. Phys. **8**, 116, 1921

quency value $\nu = 39801$ and $\nu = 26620.7$. If in the normal atom of magnesium one of the two electrons were in one of these two levels, the first one, that corresponding to the smallest potential energy, would naturally be its most probable location. The actual jump of this electron would then be from this M_{III} or 3(2,2) level to the L_I or the 2(1,1) level. Even if, in the normal magnesium atom, no electron is in a 3_2 level (Bohr places the two outer magnesium electrons in 3_1 orbits) yet an electron, once removed from the L_I level, would have to return to it through a 3_2 level, and in accordance with all spectroscopic behavior the most likely line to be excited would be that corresponding to the smallest permitted energy change. This would be the change to L_I from $\nu = 39801$. We can, then, locate with the aid of Eq. (1) this L_I level from our observed line at λ 231.6 ($\nu = 431{,}800$) and the M level at $\nu = 39801$.

Thus $\nu_{LI} = 471{,}600$ and $\nu_{LI}/R = 4.298$; $\sqrt{\nu_{LI}/R} = 2.073$.

When the position of this L_I level for magnesium is compared with the position of the same L_I level just found for sodium and with that computed from the Horton and Davies value of the third or highest ionization potential of neon, namely 22.8 volts, which gives $\nu_{LI} = 184{,}680$, $\nu_{LI}/R = 1.683$, $\sqrt{\nu_{LI}/R} = 1.297$, the straight line relation shown in Fig. 1 is obtained. This may be taken as an excellent indication that these three L_I levels are correctly located and also as justification of the foregoing statement that all three observed L lines of magnesium are accurately predicted by the Bohr theory.

Aluminum

Plate II and the spectrum labelled O in Plate I show the lines obtained with "chemically pure" aluminum electrodes. In these photographs the strong carbon, silicon, and hydrogen lines appear faintly and the oxygen lines, identical with those found with magnesium, very powerfully. Plate III however brings out the characteristic Al lines much better, though boron and fluorine lines are also present here. All of the lines in any of these plates which either are or may be due to aluminum are given in Table X. It is noteworthy that of the very few aluminum lines below 1000 A, the two at 695.9 A and 856.8 A have very recently been predicted precisely as here found, by Paschen[9] through the working out of the spectrum due to the aluminum atom when stripped of all of its valence electrons, Al(III). It is remarkable also that all of our strongest aluminum lines like those at 1353.0 A, 1379.7 A, 1384.5 A, 1605.9 A, 1612.0 A, 1854.7A, and 1862.7 A belong to Al(III), which seems to show that the aluminum atoms exist most abundantly in our sparks

[9] Paschen, Ann. der Phys. **71**, 152, 1923

in this entirely stripped state. The only good plate which goes down to 136 A shows two scarcely mistakable lines at 136.6 A and 144.3 A which were originally thought to be the strongest lines of the L spectrum of aluminum and were so reported in a preliminary communication, but for theoretical reasons to be presently detailed, we have been obliged to conclude that these two lines are due to oxygen. Between the lines at 144.3 A and 230.8 A there are found a number of very faint lines about the reality of some of which there was some uncertainty. Each of us measured these lines independently before we had made any theoretical calculations whatever and retained only those upon which we agreed. We then found that four of the seven lines thus obtained gave very strong theoretical evidence that they belonged to the spectrum of aluminum. This evidence is as follows.

TABLE X

Aluminum

Int.	λ	ν		Int.	λ	ν	
0	136.6	732332	O	4	1379.7	72478	*III*, $3p_2-4s$
0	144.3	692809	O	4	1384.5	72229	*III*, $3p_1-4s$
0	162.4	615839	?	0	1540.3	64921	
0	186.9	534988	?	5	1605.9	62272	*III*, $3p_2-3d$
0	200.0	499950	?	5	1612.0	62036	*III*, $3p_1-3d$
0	219.1	456413	? O	4	1671.0	59844	
0	221.5	451508	? O	3	1721.0	58105	*II*, $3p_2-3d$
0	225.9	442693	? O	2	1725.6	57950	*II*, $3p_1-3d$
0	230.8	433332	?	0	1750.4	57129	
0	656.7	152270	O_1	2	1760.7	56797	*II*
0	658.4	151879	O_1	2	1764.4	56676	*II*
1	695.9	143707	*III*, $3s-4p$	2	1768.4	56549	II
0	802.0	124694	O_1	0	1774.2	56365	
0	856.9	116707	*III*, $3p_1-5s$	0	1777.5	56258	
0	1264.8	79066	Si_1	0	1818.8	54980	
1	1343.5	74435	O	10	1854.7	53917	*III*, $3s-3p_1$
1	1353.0	73909	*III*, $3d-5f$	10	1862.7	53685	*III*, $3s-3p_2$

In the normal atom of aluminum the 3 outer or M electrons are according to Bohr[10] in the 3_1 and 3_2 levels. When, then, an L electron is knocked out it is to be expected that it will be most frequently replaced by a jump from a 3_1 or a 3_2 level. But in normal aluminum no 3_1 level has been observed spectroscopically,[6] so that the jump to be expected most frequently is that from the observed 3_2 level having a frequency value of 48168[5] to the L_I or the L_{II} L_{III} levels. Assuming that both of these jumps occur we can find at once from the Kossel relation the frequency values of these two levels (the L_{II} L_{III} levels are so close together at this value of atomic number that our plates would not resolve them) as soon as we have an observed line corresponding to these jumps. Computing in this way, with the use of the lines at 162.4 A and 200.0 A, we ob-

[10] Bohr, Ann. der Phys. **71**, 260, 1923

tain $\nu_{LI} = \nu_{162.4} + \nu_{MIII}$; $\nu_{LI} = 615{,}800 + 48{,}168 = 664{,}000$. Similarly $\nu_{LII\ LIII} = \nu_{200.0} + \nu_{MIII}$; $\nu_{LII\ LIII} = 500{,}000 + 48{,}168 = 548{,}200$.

But if the foregoing assumptions are correct it should be possible to find other jumps to these same levels. Thus we already know that Al(III) exists in our source and Paschen has recently worked out fully its spectral series and located its $3_1\ 3_2\ 3_3$ levels at frequencies of 229,450, 175,690, and 113,500. By analogy with sodium, in which we found the jump from the 3_1 level to the L_I level the only one which appeared on our plates, it will here be assumed that the most likely jump in Al(III) will be to L_I from $\nu = 229{,}450$. Combining this frequency with that of the observed line at 230.8 A we have $\nu_{LI} = \nu_{230.8} + \nu_{MII}$; $\nu_{LI} = 433{,}300 + 229{,}450 = 662{,}800$, which agrees within one part in 600 (better than our observational error) with the L_I level as located from the use of line 162.4 A.

Again there is another observed level in the Al(I) spectrum, namely that at 15,845,[5,6] which corresponds to the 3_3 orbit. The only jump permitted by the selection principle from this level is to the L_{III} level.[2] Assuming that this jump gives rise to our line at 186.9 A we have $\nu_{LIII} = \nu_{186.9} + \nu_{MV}$; $\nu_{LIII} = 535{,}000 + 15{,}845 = 550{,}800$.

The agreement between this result and the foregoing computation of the L_{III} level from the use of line 200.0 A is not quite as good as in the case of the L_I level, but an error of .4 A in our measurement of each of the lines would account for the difference. With very faint lines such as these are such an error is admissible, though scarcely with the stronger and sharper lines. Taking the means of each set of determinations of levels we have then the following final values for aluminum:

$$\nu_{LI} = 663{,}400;\ \nu_{LII\ LIII} = 549{,}500.$$

We can now obtain an entirely independent check upon these levels as follows. We have: $\nu_{LI}/R = 6.045$; $\nu_{LII\ LIII} = 5.008$; $\sqrt{\nu_{LII}/R} = 2.459$; $\sqrt{\nu_{LII\ LIII}/R} = 2.238$. Fig. 1 shows that the value of the L_I level thus obtained is exactly where an extrapolation from the corresponding levels found above for neon, sodium, magnesium would place it. The evidence then that we have now correctly located this level is quite satisfactory. Our $L_{II}\ L_{III}$ level for aluminum will be seen from the lower line of the figure to be a trifle higher than an extrapolation from the corresponding levels in neon and magnesium would place it. This raises some question as to the correctness of our determination of the $L_{II}\ L_{III}$ level in aluminum. The four lines at 230.8 A, 200.0 A, 186.9 A, and 162.4 A are the only ones of the seven observed lines in this region which seem to be obtainable from any possible jumps in the aluminum atom, although the Al(II) levels very recently worked out by Paschen[11] have been tried. If the L_I

[11] Paschen, Ann. der Phys. **71**, 537, 1923

level has been correctly obtained in the foregoing, then it is improbable that any lines exist in the L spectrum of aluminum of higher frequency than the frequency value of the L_I level, namely $\nu = 663400$ or λ 151 A. Since the lines at 136.6 A and 144.3 A are both of higher frequency or shorter wave-length than these values, they cannot be due to the knocking of a single electron from the L ring of aluminum. As indicated above, therefore, we think it probable that these two lines are due to oxygen, which is furnishing practically all the strong lines below 1000 A, though they may possibly be due to the removal of two electrons from the L shell of the aluminum atom.

Silicon

Table XI and Plate III show the lines due to silicon. These were obtained both from the use of the element as electrodes and from that of sodium silicate. The twelve lines indicated by "IV" all belong to the

TABLE XI

Silicon

Int.	λ	ν		Int.	λ	ν	
1	361.6	276549	$IV, 3s-5p$	0	1194.4	83731	C_2
1	392.7	254647		5	1206.5	82884	
3	457.7	218503	$IV, 3s-4p$	0	1228.1	81425	$IV, 4p_1-6s$
0	486.6	205516		0	1250.3	79981	
2	815.0	122704	$IV, 3p_2-4s$	1	1260.5	79337	
2	818.0	122257	$IV, 3p_1-4s$	1	1264.9	79056	Al
0	994.6	100540		1	1294.9	77228	
0	997.5	100251		2	1299.0	76981	
0	1066.7	93746	$IV, 3d-4f$	1	1303.5	76717	
0	1086.9	92005	?	0	1309.5	76368	?
2	1108.9	90177		6	1393.9	71742	$IV, 3s-3p_1$
2	1110.3	90064		6	1403.0	71276	$IV, 3s-3p_2$
2	1113.5	89807		0	1416.8	70583	
2	1122.6	89083	$IV, 3p_2-3d$	0	1500.9	66625	
2	1128.4	88623	$IV, 3p_1-3d$	0	1526.9	65493	?C
1	1143.3	87466		0	1533.4	65213	$IV, 4d-6f$
1	1164.0	85908	?				

spectrum of the silicon atom completely stripped of its valence electrons Si(IV) as very recently worked out by Fowler.[12] It is to be noted that all the strongest lines belong to this completely stripped silicon atom thus indicating that, as in the case of aluminum, this type of ionization is extremely common in our vacuum sparks.

Phosphorus

The phosphorus lines were obtained from aluminum electrodes having phosphorus in their cores and also from a flux of borax and sodium phos-

[12] Fowler, Roy. Soc. Proc. **103**, 423, 1923

phate fused into aluminum electrodes. Table XII and Plates III and IV show the spectra thus obtained.

The tables already published by Paschen[9] and by Fowler[12] giving the experimental progression of the series terms for Na(I), Mg(II), Al(III), Si(IV) should make it possible to extrapolate from this progression to P(V) and thus to find lines to be expected from phosphorus when stripped of all of its valence electrons. Thus the level corresponding to the convergence frequency of the fundamental series (3_3) is $12{,}800\times25=320{,}000$, that of the diffuse series (3_2) is $17{,}450\times25=436{,}250$, and that of the principal series (3_1) $21{,}200\times25=530{,}000$. From these extrapolations the first term of the principal series ($3s-3p$) is $\nu=93{,}700$, and that of the

TABLE XII

Phosphorus

Int.	λ	ν		Int.	λ	ν	
3	824.5	121292		1	997.9	100211	
3	827.9	120789		1	999.4	100062	
1	847.6	117984		1	1002.8	99721	
3	855.5	116891		1	1015.3	98491	
4	859.6	116335		1	1025.3	97530	H
0	865.5	115541		0	1027.9	97282	
2	871.3	114771	$V,\ 3p_2-3d$	3	1030.3	97056	
2	877.4	113968	$V,\ 3p_1-3d$	1	1032.9	96817	
1	908.2	110112		1	1035.3	96589	
1	913.8	109431		5	1117.9	89457	$V,\ 3s-3p_1$
2	916.8	109077		3	1127.8	88670	$V,\ 3s-3p_2$
2	918.4	108891		0	1153.6	86687	
1	921.7	108494		1	1198.7	83423	O
6	950.6	105202		0	1287.9	77649	
3	964.5	103676		0	1646.5	60737	

diffuse series ($3p-3d$) is $\nu=116{,}250$. Similarly the progression of the doublet separation for Na(I), Mg(II), Al(III), and Si(IV) as given by Fowler makes it possible to obtain by extrapolation the doublet separation for P(V) which thus is found to be about 800 cm.$^{-1}$. Two of the strongest doublets in our phosphorus spectrum, namely those at λλ 871.3, 877.4; $\nu=$ 144,771, 113,968, and λλ1117.9, 1127.8; $\nu=89457$, 88670 have the correct separation and are in the correct position within the limits of uncertainty of our extrapolation. It is hoped that further series relationships can soon be worked out.

SULPHUR

The sulphur spectrum was obtained from the element in aluminum tubes and also from sodium sulphate in such tubes. It will be seen to be characterized by a very large number of lines (see Table XIII and Plates III and IV) as is to be expected from the large number of its valence electrons combined with the foregoing evidence that from one to all of

these may be stripped off in our vacuum sparks, each of course thus adding a new set of series. Series relationships ought to be obtainable from the pursuit of the method indicated under phosphorous but the search obviously becomes more and more difficult with increasing complexity of spectra.

TABLE XIII

Sulphur

Int.	λ	ν		Int.	λ	ν	
0	370.2	270124		1	758.5	131843	
0	439.1	227744		5	764.7	130779	
0	465.2	214943		4	774.2	129164	
0	476.5	209864		5D	786.6	127133	
1	485.0	206194	O	2	790.0	126587	
1	500.4	199856		4	796.9	125483	
1	521.1	191909		3	800.1	124981	
0	539.6	185340		3	804.3	124327	
2	551.0	181485		5	809.2	123585	
2	554.0	180512	O	3	816.0	122546	
0	560.3	178845		2	824.5	121292	
0	564.3	177208		2	827.0	120915	
0	568.3	175957		2	837.0	119474	
0	572.0	174831		2	841.1	118895	
0	577.7	173115		2	844.0	118478	
0	585.2	170885		1	849.2	117754	
0	594.1	168325		2	852.6	117283	
0	607.9	164498		2	854.8	116988	
3	611.4	163564		1	857.6	116604	
0	628.0	159243		1	860.6	116205	
1	641.3	155941		2	866.9	115356	
1	646.7	154631		0	890.8	112260	
4	652.9	153172		2	894.9	111751	
4	654.6	152772		2	907.0	110251	
4	656.6	152295		2	911.4	109720	
3	658.5	151863		2	915.3	109256	
5	661.4	151188		2	919.3	108784	
3	665.3	150310		1	924.2	108198	
1	669.7	149330		1	933.7	107105	
3	675.0	148159		3	937.7	106642	
4	677.4	147628		1	945.0	105826	
5	679.9	147083		0	971.0	102983	
4	682.1	146608		1	978.2	102231	
1	692.0	144502		0	981.9	101846	
2	696.2	143635		1	996.3	100373	
4	699.2	143019		5	1014.8	98544	
4	701.4	142576		5	1021.3	97919	
4	703.7	142110		2	1031.5	96951	
3	707.9	141271		0	1050.3	95213	
4	711.0	140639		3	1063.0	94075	
4	716.9	139484		3	1073.4	93161	
4	722.0	138498		2	1077.6	92798	
4	725.2	137887		0	1190.5	84002	
5	729.4	137097		1	1194.0	83752	
2	735.1	136038		4	1200.8	83275	
3	741.6	134845		1	1204.6	83015	
5	745.2	134192		0	1250.2	79990	O
5	749.5	133424		1	1253.7	79763	
3	753.8	132668		3	1259.3	79409	

CHLORINE

The chlorine spectrum was taken with sodium chloride and borax in aluminum electrodes. Sodium, aluminum, and boron have practically

no lines in the region studied, while the oxygen lines are well known. The chlorine spectrum has, like the sulphur, a multitude of strong lines. Results are shown in Table XIV and Plates III and IV.

TABLE XIV

Chlorine

Int.	λ	ν		Int.	λ	ν	
1	528.3	189294		6	960.4	104121	
4D	536.7	186327		2	973.0	102771	
0	542.5	184318	? C	4	977.2	102335	C
2	549.7	181907		4	984.8	101546	
3	553.1	180789	? O	3	1005.4	99461	
4	556.4	179714		4	1008.6	99145	
4	561.5	178094		4	1014.9	98535	
3	565.1	176966		3	1063.6	94019	
3D	569.7	175537		3	1068.2	93615	
4D	574.3	174122		4	1070.9	93381	
3	584.6	171057		3	1079.0	92683	
4	586.9	170384		0	1128.0	88655	
3	591.5	169071		2	1145.0	87336	
3	595.8	167833		0	1200.5	83296	
3	606.3	164938	F	2	1302.0	76807	
3	609.3	164112		2	1305.1	76623	
2	612.2	163353		2	1331.2	75120	
2	618.2	161755		1	1344.0	74405	
2	621.1	161018		3	1347.2	74230	
2	623.7	160341		2	1351.6	73984	
4D	635.8	157272		2	1354.6	73824	
3	639.1	156460		0	1418.4	70504	
4	653.7	152980		0	1428.3	70013	
4D	663.2	150780		1	1462.3	68386	
3	670.8	149080		1	1465.8	68222	
3	682.2	146585		1	1542.1	64849	
1	689.6	145022		0	1548.2	64591	C
4	707.4	141363		0	1551.2	64466	C
4	712.6	140323		0	1561.0	64061	C
4	715.8	139706		0	1565.1	63893	
5	718.7	139144	O_2	2	1577.7	63383	
2	725.4	137849		0	1590.7	62866	
3	729.4	137105		0	1593.5	62756	
2	777.5	128622		0	1656.8	60359	?
4	787.8	126936		1	1663.1	60129	?
3	793.3	126053		0	1808.0	55309	?
6D	840.9	118926		0	1812.4	55175	?
4	851.6	117426		1	1817.8	55012	
4	864.4	115690		2	1821.9	54888	
4	888.0	112618		2	1832.1	54584	
4D	893.5	111918					

POTASSIUM

The potassium spectrum was obtained from the use of potassium acid borate in aluminum tubes. In the region of wave-length which we are investigating there are of course no potassium lines due to the single electron in its N shell. Yet Table XV and Plate IV reveal a very considerable number of rather faint lines extending from 312 A up to 1303 A. These lines must then be due to the removal of some of the 8 electrons of the M shell, i.e. they may be definitely classified as belonging to the M

spectrum of potassium. In view of the complexity of this spectrum we have been unable to find any confirmations of the Bohr theory such as we found in the case of sodium.

TABLE XV

Potassium

Int.	λ	ν		Int.	λ	ν	
0	312.9	319632		0	474.9	210557	
0	341.7	292654		0	479.1	208720	
0	344.9	289922	O	1	495.1	201967	
0	355.1	281643	O_2	1	520.3	192182	
0	362.7	275748	?	2	580.6	172233	O_2
1	379.9	263227		4	600.2	166617	O_1
2	382.5	261411		3	612.5	163279	
2	390.1	256318		4	644.8	155096	O_1
2	392.7	254654		0	724.4	138045	
0	399.3	250432		1	737.0	135691	
0	402.3	248546		1	742.1	134745	
2	409.8	243998		2	745.3	134174	
2	414.4	241324		1	750.0	133326	
1	418.0	239263		1	754.6	132522	
0	422.1	236888		3	765.7	130608	
0	425.6	234984		3	778.6	128442	O_1
0	441.6	226449		3	796.8	125500	O_1
2	444.4	225043		0	873.1	114541	
2	448.5	222985		1	878.7	113801	
0	466.5	214358		1	1303.6	76711	
4	470.4	212571					

CALCIUM

The spectrum of calcium was obtained with calcium electrodes and consists, as Plate IV and Table XVI show, of a very few strong lines upon a background of a considerable number of faint ones, so faint that they scarcely show upon the plate. It is possible to fit some of these strong lines into the Bohr theory precisely in the manner used in analyzing the spectrum of magnesium. Thus the separation of the M_{II} M_{III}[13] doublet is computable as in case of the L_{II} L_{III} doublet discussed above. Thus:[7]

$$\Delta\nu_m = \Delta\nu_m(Z-s)^4$$

in which $\Delta\nu_H$, since it now corresponds to the M series instead of the L, has the value $(8/27)\times.365^{-1}$ cm. $=.108^{-1}$ cm. Inserting the separation of the strong doublet $\lambda = 655.9$ A, 669.6 A, $\nu = 152460$, 149350 and therefore $\Delta\nu_m = 3110$, and then solving for the screening constants, there results $s = 7$. The value of s given by Sommerfeld[7] for the M_{II} M_{III} doublet is $s = 8.3$. Our value is somewhat less than this as it should be because of the fact that the M shell is here not entirely full. The result is therefore close enough to the value to be expected to furnish quite satisfactory evidence that the chosen doublet is in fact the M_{II} M_{III} doublet of calcium.

[13] For notation see Bohr and Coster[2]

The frequency value of the M_{II} M_{III} levels can now be computed precisely as in the case of the L series of magnesium. We there found that the jump from the M_I level to the L_{II} L_{III} levels corresponded to our observed magnesium L doublet. Similarly the jump from the N_I level to the M_{II} M_{III} levels may be expected to correspond to the M doublet. The frequency value of the N_I level, which is the convergence frequency of the principal series of calcium singlets has the value $\nu = 49{,}305^{5\,6}$. We have then the equation $\nu_{MII} = \nu_{655.9} + 49{,}305$; $\nu_{MII} = 152{,}460 + 49{,}305 = 201{,}770$, and similarly $\nu_{MIII} = \nu_{669.6} + 49{,}305$; $\nu_{MIII} = 149{,}350 + 49{,}305 = 198{,}660$; $\nu_{MII}/R = 1.8387$; $\nu_{MIII}/R = 1.8104$; $\sqrt{\nu_{MII}/R} = 1.3560$; $\sqrt{\nu_{MIII}/R} = 1.3455$.

TABLE XVI

Calcium

Int.	λ	ν		Int.	λ	ν	
0	269.7	370769		0	727.4	137482	
0	280.9	355973		0	732.9	136450	
0	299.7	333712		0	736.3	135809	
1	322.1	310492	O, Mg	1	740.2	135106	
2	324.7	307939		0	745.9	134070	
3	331.8	301414		0	748.2	133647	
0	334.9	298570		1	773.7	129247	
4	341.0	293290		0	800.1	124989	C
2	344.7	290141		0	810.1	123435	C
0	352.9	283382		0	821.2	121769	
3	358.0	279314		0	846.5	118140	
6	403.8	247672		1	856.5	116752	
6	410.1	243837		0	875.3	114247	
0	439.7	227412		0	883.0	113255	B
0	444.1	225164		0	934.6	106997	
0	450.5	221956		0	1084.6	92198	N
0	477.5	209428		0	1286.7	77718	
0	535.1	186881		0	1434.2	69724	
3	537.8	185957	C_2	0	1454.3	68763	
1	542.2	184444		0	1464.1	68301	
1	558.1	179176		0	1485.9	67299	
0	572.0	174825		0D	1500.0	66668	
1	600.9	166406	O_1, C	5	1545.6	64700	
0	629.0	158977	O_1	5	1555.0	64307	
0	632.7	158053		4	1562.4	64005	
1	638.0	156747		0	1571.5	63635	
0	642.5	155649	C	0	1586.1	63047	
3	646.4	154708		0	1647.5	60700	
0	651.0	153610	C	0	1807.8	55315	
5	655.9	152465		0	1814.8	55103	
4	669.6	149347		10D	1838.9	54382	
0	688.6	145222					

Bohr and Coster,[2] who had no data sufficiently accurate to enable them to differentiate between the two levels, give the value of ν/R for these levels as 2.0. Their probable error as may be seen from their series of values, is of the order of .5, so that our results are in complete agreement with preceding estimates of these levels and actually for the first time fix their values accurately.

The foregoing is the only certain success which has yet been reached in the fitting of the calcium spectrum into the Bohr theory, but the simplicity of the spectrum and the strength of the main lines make it an alluring one for further studies of this sort. The many faint lines are almost certainly, and some of the stronger very probably, due to the removal of more than one of the 8 electrons which are in the M shell of calcium.

TABLE XVII

Chromium

Int.	λ	ν		Int.	λ	ν	
1	202.6	493486		2D	585.1	170923	
1	207.2	482556		3	595.5	167920	
0	214.9	465441		2	599.5	166803	O_2
0	222.6	449297	?	2	608.3	164398	O_2
1	226.4	441677		5	613.8	162927	
0	231.7	431667	? O_2	6	619.9	161324	
2	238.6	419182	O_2	6	629.9	158763	
1	253.8	393964		5	634.0	157736	
1	263.1	380055		6	637.8	156796	
2	269.8	370617		1	643.5	155393	O_2
0D	278.0	359777		4	648.7	154159	
0	294.9	339121	? O_2	4	654.9	152704	
1	308.1	324570		3	661.0	151291	
1	322.0	310569	O_2	5	667.1	149896	
1	328.4	304535	O_2	3	673.4	148507	
3D	336.3	297345		4	677.6	147575	
0	345.3	289645	O_2	5	681.3	146785	
2	352.2	283913		4	687.7	145423	
0	361.3	276775		5	694.7	143953	
1D	369.7	270482		3	706.1	141619	
1	378.1	264459		2	710.0	140837	
1	384.1	260362		3	712.6	140339	
0D	394.0	253807		1	724.6	138007	
0	402.2	248633		1	728.6	137242	
4	434.6	230118	O_2	3	745.0	134225	
4	438.3	228149		2	749.7	133385	
4	456.8	218924		1	754.1	132608	
4	464.0	215499		4	764.4	130830	
4	469.8	212847		2	768.2	130171	
0	475.4	210362		3D	780.1	128192	
0	483.4	206864	?	3	786.0	127225	
0	487.7	205031	?	2	790.2	126555	
2	498.0	200803		2	796.2	125590	
2	508.0	196866	O_2	1	803.6	124435	
2D	515.7	193930		2	808.9	123619	
2D	524.3	190749	O_2	1	815.2	122668	
3D	531.1	188285		1	818.4	122193	
2D	540.0	185199	O_2	0	825.3	121171	
1	547.0	182812		0	850.9	117525	
1	553.6	180646	O_2	1	854.3	117049	
1	563.0	177620		0	877.5	113967	
5	575.3	173816					

CHROMIUM AND COPPER

The spectra of chromium and copper obtained from the pure metals are shown in Tables XVII and XVIII. Plate II also gives the reproduction of the copper spectrum.

TABLE XVIII

Copper

Int.	λ	ν	Int.	λ	ν	
0	155.7	642426	1	426.1	234670	
0	159.4	627392	1	433.0	230942	
0	164.6	607718	1	438.9	227822	
0	169.7	589449	3	444.0	225240	
0	186.1	537403	4	446.6	223934	
0	189.2	528625	2	450.5	221985	
0	198.5	503804	7	452.8	220858	
0	200.6	498405	3	459.2	217761	C
0	203.8	490653	5	464.3	215401	
0	207.2	482672	2	467.2	214037	
1	210.9	474203	3	472.5	211663	
0	215.5	464123	3	476.2	210005	
0	219.7	455083	1	481.9	207503	
0	235.4	424773	4	484.5	206411	
0	237.9	420433	4	491.8	203326	
0	241.9	413411	1	494.4	202278	
1	248.5	402447	3	496.9	201260	
1	252.9	395382	4	499.6	200176	
2	255.0	392126	8	505.4	197883	
1	259.1	385907	1	509.1	196413	
1	262.4	381112	0	513.7	194681	
1	268.8	371996	0	516.5	193611	
1	270.1	370247	0	521.0	191946	
0	272.6	366811	0	523.8	190916	
0	274.9	363782	0	526.9	189786	
0	278.6	358976	0	531.8	188048	
2	281.6	355151	0	536.8	186296	
1	283.6	352572	2	540.7	184952	
0	286.5	349065	2	542.4	184379	
0	297.2	336462	2	547.1	182795	
1	299.5	333890	2	548.5	182309	
1	304.2	328785	2	550.8	181551	
1	306.7	326052	1	553.1	180789	
1	310.1	322529	1	555.8	179914	
1	312.4	320061	1	559.5	178731	
6	324.5	308157	0	568.1	176041	
5	329.2	303739	1	573.1	174496	
4	333.2	300165	1	584.6	171054	
4	335.8	297796	0	588.4	169941	
3	339.8	294325	1	598.4	167118	
3	342.6	291903	1	602.7	165915	
3	345.4	289528	1	606.0	165014	
3	348.2	287175	0	609.4	164101	
3	350.5	285339	0	611.2	163613	
1	353.6	282821	2	615.8	162388	
1	355.3	281429	2	619.9	161311	
5	358.0	279298	0	623.1	160485	
4	361.0	277031	0	624.9	160038	
2	364.0	274725	0	642.3	155683	C_3
1	367.0	272502	0	649.1	154057	
2	371.4	269244	0	657.6	152059	
1	374.7	266880	0	662.3	150998	
2	377.6	264816	1	666.4	150067	
3	379.3	263630	1	672.1	148790	
1	387.5	258098	3	676.5	147828	
2	405.9	246372	3	682.1	146600	
0	408.8	244630	3	687.6	145427	C_3
0	411.2	243214	3	691.2	144672	
0	413.5	241834	1	693.0	144292	
1	418.1	239160	3	700.1	142841	
0	422.6	236636	1	712.2	140416	

Copper (Cont'd)

Int.	λ	ν	Int.	λ	ν	
3	715.3	139796	2	808.7	123663	
2	719.4	139014	2	813.3	122953	
1	723.6	138202	2	833.1	120028	O_3
3	730.3	136934	2	836.0	119624	O_3
2	731.9	136623	1	840.7	118948	
2	735.0	136049	2	844.4	118427	
2	743.4	134510	2	858.1	116541	C_3
0	750.7	133214	1	868.8	115101	
0	753.9	132640	2	872.3	114639	
1	758.6	131830	2	875.1	114271	
0	767.4	130312	2	878.4	113842	
5	777.3	128657	1	884.2	113097	
6	788.3	126860	1	887.3	112703	
4	791.4	126354	1	890.2	112338	
2	792.8	126138	2	893.8	111883	
2	797.5	125400	1	896.7	111521	
3	801.0	124849	2	900.1	111102	
3	803.2	124504				

It will be noticed that the copper extends on our plates down to 155 A the four lines of lowest wave-length appearing very definitely and exactly measurably on both sides of the central image. Since the M_{II} M_{III} levels of copper as computed by Bohr and Coster and Sommerfeld from x-ray measurements in the K series (K absorption edge and K_β line) are at 175 A, according to Bohr, and 186 A according to Sommerfeld, while our observed lines run down to 155 A, it is clear that our plates show practically the complete M spectrum, including the jumps to the M_I level, which is of course somewhat farther down in wave-length than the M_{II} M_{III} levels.

The same is of course true in the case of chromium whose M_{II} M_{III} levels are predicted by Bohr and Sommerfeld at 260 A and 276 A respectively while our chromium lines go down to 202.6 A.

This means that our method is capable of revealing the full M spectra of all the elements up to copper (atomic number 29) and that we have observed them all save for a few omissions above 20. It is interesting that the crystal spectrometer is at present capable of going down to the same point, copper, in the L series.

Copper is furthermore the first element in which the M levels are all full.[2] The fact that its M spectrum consists of an enormous number of lines extending from 155 A clear up to the visible (our plates themselves stop at about 900 A merely because of the way in which they happened to be taken) indicates that many of its 18 M electrons are removed in our sparks, each one of them giving rise to its characteristic series of lines. Since it is the first element in which the M shell is full the M electrons may be expected to be very lightly held.

The Progression of Spectra with Atomic Number

Plates I, II, III and IV all reveal directly a progression of spectra with atomic number in this ultra-violet region which is quite like the progression discovered by Moseley in the hard x-ray region.

Plate I for example, the magnification in which is about 2 fold, shows the most powerful line in each of the L spectra of the elements from boron to fluorine progressing systematically toward shorter and shorter wave-lengths as indicated by the arrows. In the case of boron the strongest line is just off the plate; in the case of carbon that line is undoubtedly at 1335.0 A. In the case of nitrogen it is at 1085.2 A, in oxygen it is unquestionable at 834.0 A, in fluorine it is 656.4 A (other fluorine plates bring this out much more sharply than does the one here given which was preferred for other reasons.) Each spectrum has in general few if any strong lines of longer wave-length than this line of maximum intensity.

Plate II, the magnification of which is about 10 fold, shows the same sort of progression of the L spectra of sodium, magnesium and aluminum.

Plate III, of magnification about 2, illustrates very satisfactorily the progression of the M series through magnesium, aluminum, silicon, phosphorus, sulphur and chlorine.

Plate IV, of magnification 3.5, reveals beautifully the progression of the M series through phosphorus, sulphur, chlorine, potassium and calcium even though this series of elements runs right through argon which should come in between chlorine and potassium.

When Moseley brought to light such a progression in the hard x-ray field, he plotted merely the square root of the frequency of the strongest observed lines to obtain his relation between frequency and atomic number. If we adopt the same procedure arbitrarily calling this line $L\alpha$ in conformity with the convention which one of us previously adopted,[1] we obtain a spectroscopic progression (see Fig. 2) which in the case of both the K and the L series is complete from hydrogen to uranium barring only a few short gaps. These gaps, however, are in straight portions of the curves and hence intermediate points can be accurately determined by interpolation.

In this plotting there is in general no ambiguity about which line to call the strongest line. In sodium, for example there is but one certain line of the L series and this corresponds to the lowest permissible energy jump into the L_I level. In the case of magnesium and of aluminum there are two lines of intensities quite comparable, and we have taken in each case the one of these which corresponds, as in the case of sodium, to the lowest energy jump to the L_I level. Similarly for neon, upon which we

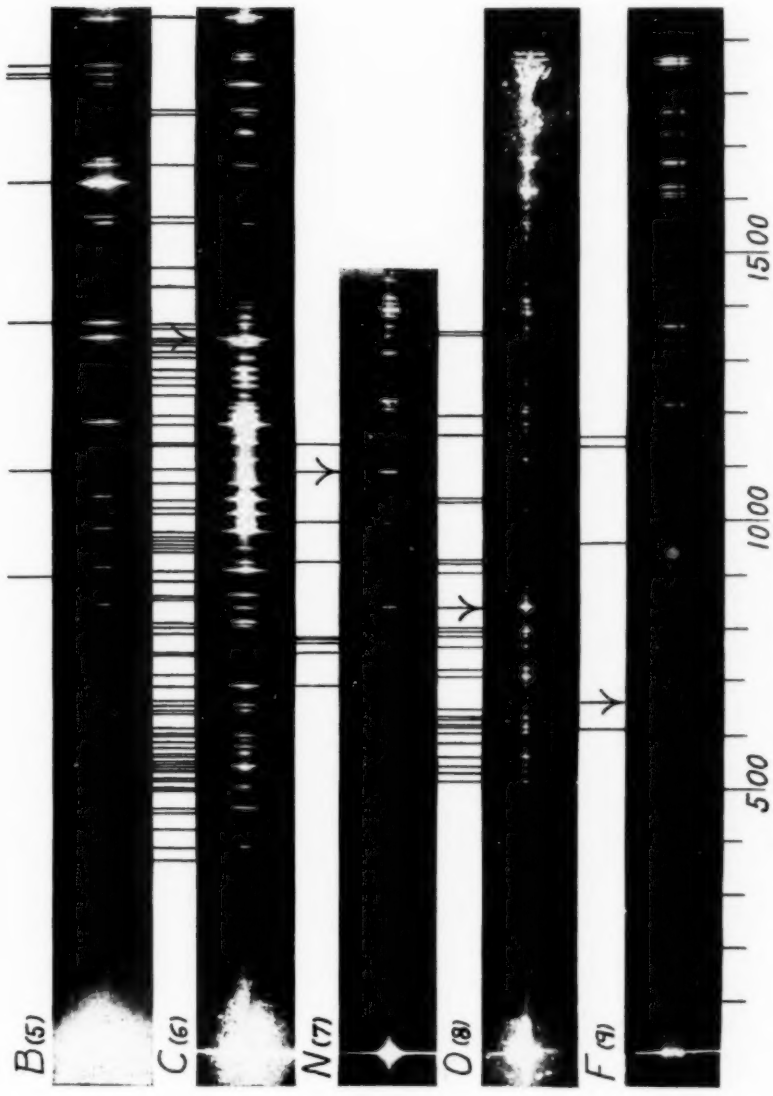

PLATE I. Spectra of boron, carbon, nitrogen, oxygen and fluorine.

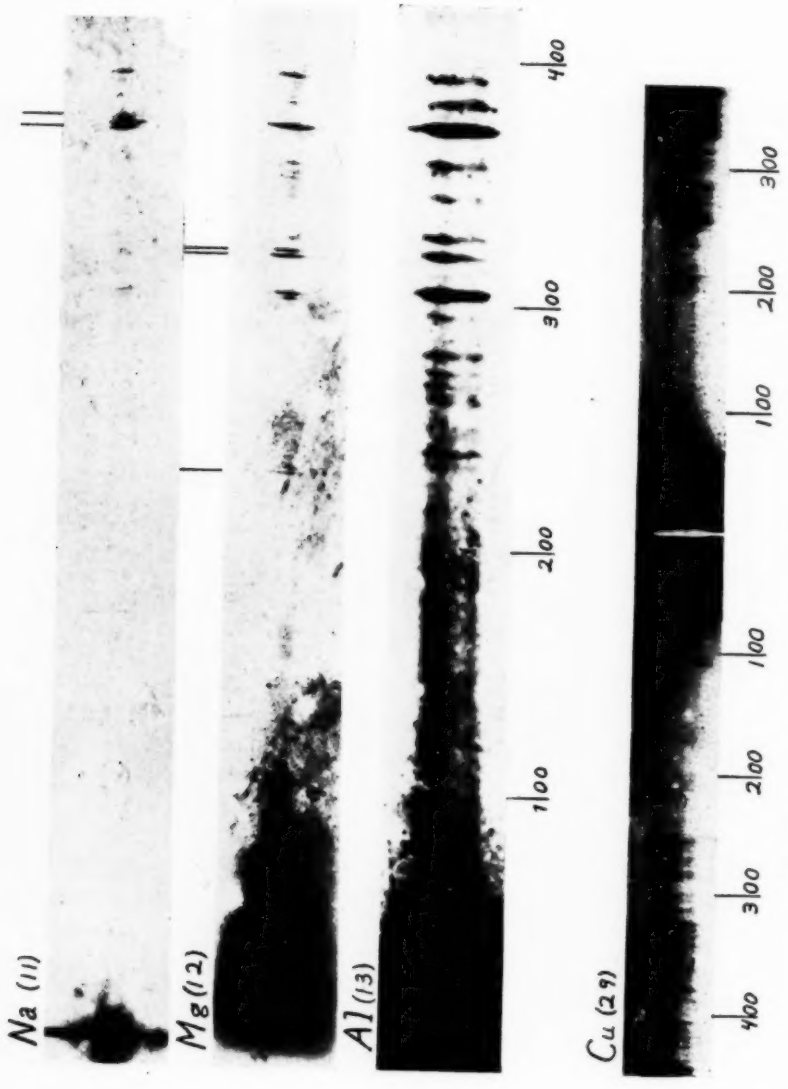

PLATE II. Spectra of sodium, magnesium, aluminium and copper.

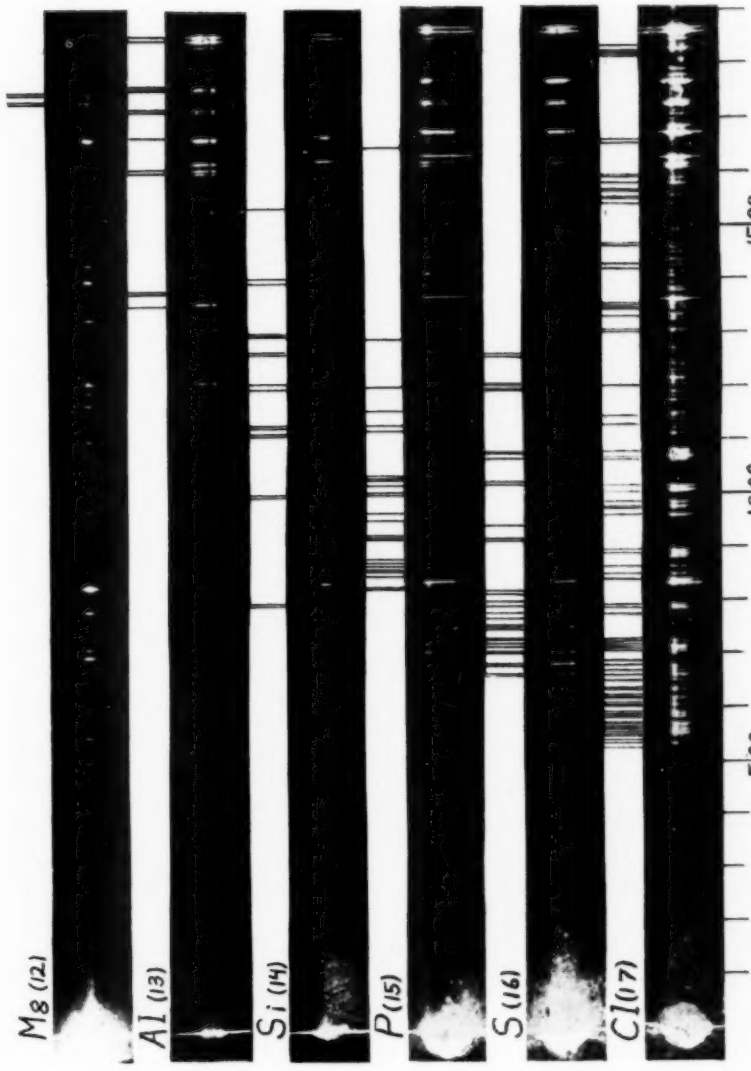

PLATE III. Spectra of magnesium, aluminium, silicon, phosphorus, sulfur and chlorine.

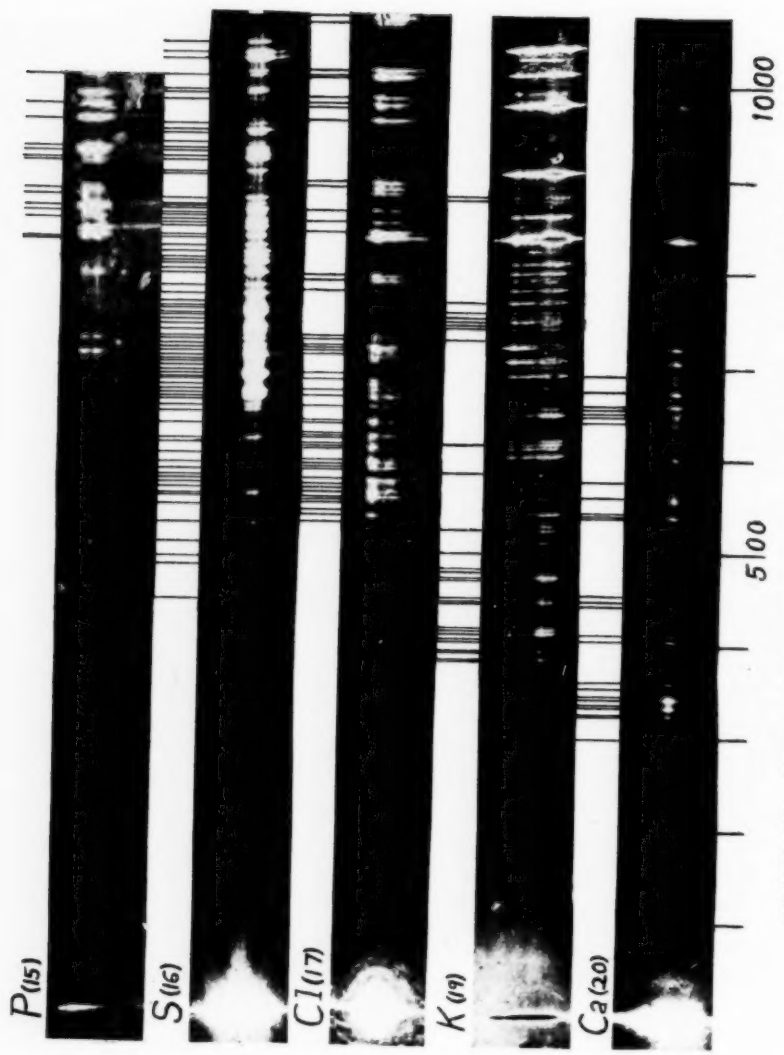

PLATE IV. Spectra of phosphorus, sulfur, chlorine, potassium and calcium.

have made no measurements ourselves, we have plotted that one of the Horton and Davies radiation potentials which should correspond to this jump, namely that at 17.8 volts, $\nu = 144180$.

These remarks illustrate the fact that there is no completely consistent way of carrying through a Moseley progression so long as we attempt to plot any particular line, a fact brought to light quite sharply by the observation that there appears on our plates no L_{II} L_{III} doublet in sodium, for example, at all. We have thought it worth while, however, to retain Fig. 1 for the sake of exhibiting in a general way the progression of spectra throughout the whole range of the elements, a result which for the present can be best attained by plotting merely the strongest line of the L series, a line which we have arbitrarily called Lα, without, however, implying any relationship to any of the confused conventions now in use by various authors in the designation of particular lines as α_1, α_2, α_3, β_1, etc.

The ultimate exhibition of spectral progression will be through the plotting of levels or absorption edges rather than of lines and our Fig. 1 extends this type of relationship already used by Bohr and Sommerfeld to a group of elements for which these have not before been accurately known, but no completeness of progression through the elements is yet possible in this way.

Atoms Stripped of All Valence Electrons

The recent work of Paschen and Fowler in definitely working out the series corresponding to Al(III) and Si(IV) and the evidence presented above that the lines of these series appear with extraordinary intensity in our sparks makes it highly probable that in the elements from lithium to fluorine also, all of the valence electrons are frequently stripped from the atom, for exactly the same causes must operate in the two cases. This inference is somewhat strengthened by the regular progression of the very intense line which we have called the Lα line in going from lithium to fluorine. In lithium there is but one valence electron and the strongest lithium line is here definitely known to be due to the jump of this electron to the position of minimum energy from the next lowest energy level. It is this "hydrogen-like" spectrum which we are here designating as the spectrum due to the atom stripped of valence electrons. It is in fact the spectrum due to one single electron moving between the series of levels characteristic of a nucleus of unchanging charge which holds a single electron in its influence. This series of lines is of course the same so far as wave-length is concerned whether that electron has been entirely

removed and is at the observed instant giving off radiations because it is returning from infinity by jumps to its most stable orbit, or whether it has never left the atom but has simply been displaced from this most stable orbit to one or another of its possible states of higher potential energy. This latter case would correspond indeed to a larger intensity of the longest wave-length line of the series and is perhaps more likely to represent the actual behavior of the electron in the production of the spectra which we are considering, but for the sake of having a single notation to represent this series of wave-lengths alone we are here designating both cases as the spectrum due to an atom stripped of its valence electrons.

In the case of beryllium by far the strongest lines in the spectrum of our sparks, taken in the optical region with the quartz spectrograph, is the pair at 3130.55 A and at 3131.19 A which is definitely known to be due to the "stripped atom" i.e. to ionized beryllium.[14]

The strongest line on our plates due to boron is a very powerful pair at 2066.2 and 2064.2 A. This pair is reported by Eder and Valenta as a very weak "spark line." That it is by far the strongest line on our plates, which in general also show the highly ionized lines like those of Al(III), Si(IV), P(V), etc., in extraordinary strength is evidence in itself that this line is due to B(III), i.e., to the stripped boron atom

If then the strongest lithium, beryllium and boron lines are all due to stripped atoms, the unmistakable progression between these lines and the most powerful line in each of carbon, nitrogen and oxygen, points to the conclusion that this line which we have called Lα in all these substances is due to "stripped" atoms, for such progression is to be expected among "hydrogen-like" atoms of continually increasing nuclear charge.

This evidence is further supported by the similarity in character of these lines which we have called Lα lines. If these lines are all due to "stripped" atoms they should all be doublets, since the strongest line in all "hydrogen-like"* spectra is a doublet, and the value of $\Delta\nu$ for these doublets should increase systematically with increase in atomic number. Thus in the M series we now have definite knowledge not only of the existence of this characteristic doublet in the spectra of the "stripped" atoms of the elements from sodium to phosphorus, but the following table shows the progression in the frequency separation (in cm^{-1}) of this doublet, the

[14] Paschen-Gotze, Serien Gesetze der Linien Spectrum, p. 71.

*This term is used following Sommerfeld to designate spectra due to but one valence electron.

data on Al(III) and Si(IV) being taken from the papers of Fowler and Paschen while the separation of the phosphorus doublet is taken from our own plates.

	Na(I)	Mg(II)	Al(III)	Si(IV)	P(V)
$\Delta\nu =$	17	92	238	460	795

Now in the case of lithium and beryllium the line which we have called Lα is without any ambiguity a doublet due to a "stripped" atom. In the case of boron, in view of the Sommerfeld law of the alternation of doublets and triplets in going across the periodic table, the only possible doublets due to boron must be, first, an arc doublet in the spectrum of B(I), and, second, a spark doublet in B(III). Our doublet at 2064 A is definitely a spark line, and furthermore it has not the separation of the arc doublet. Hence it must be due to a "stripped" boron atom.

Again, for the reason just given, carbon can have doublets only in C(II) and C(IV). Our Lα line at 1335.0 has now been definitely measured as a doublet by both Simeon[15] and Hopfield[16] with the average separation given in cm^{-1} in the following table.

	Li(I)	Be(II)	B(III)	C(IV)
$\Delta\nu =$	.34	6.6	47	67

It is the progression in separation and in wave-length which must be depended upon for the evidence that this is actually due to C(IV) rather than to C(II). The evidence for stripped atoms up to and including carbon is then exceedingly strong.

When the foregoing was written we felt that we were probably justified in inferring stripped atoms also in the case of nitrogen, oxygen and fluorine, especially since Lyman had reported both the line at 834.0 A and that at 1085 A as doublets. Hopfield and Leifson's[16] recent finding that these two lines were both triplets was, however, definitely in conflict with our inference, since if these lines were due to stripped O and N atoms they would of necessity be doublets. Accordingly we have just taken new plates using a very narrow slit (.02 mm) and obtaining very satisfactory spectra of these lines in both the third and fourth orders. The evidence of these plates is conclusive that both of these lines have a more complicated structure than that of a doublet, 834.0 showing clearly

[15] Simeon, Roy. Soc. Proc. **102**, 488, 1923
[16] Hopfield, Astrophys. J. **53**, 62, 1923

seven components and 1035 showing four. *This is conclusive evidence that these two lines are not due to stripped atoms.*[17]

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA, CALIFORNIA,
September 15, 1923.

[17] This paragraph added January 12, 1924.

SPECTRAL SERIES IN THE SOFT X-RAY REGION

By Gerhard Krohn Rollefson*

Abstract

Critical radiation potentials for iron, determined photo-electrically.—Electrons were accelerated from a filament heated by a constant current, to an iron plate, and the photo-electric effect of the radiation excited on a plate carefully shielded from stray electrons, was measured. All surfaces exposed to the radiation were of metal and were maintained at definite potentials, and the tube after thorough baking was maintained at a pressure of 10^{-6} mm or less during measurements. (1) *M series, 40 to 175 volts.* Nine critical potentials were observed, the corresponding ν/R values being 3.46, 6.03, 7.05, 8.21, 9.63, 10.40, 10.88, 11.33 and 11.83, where R is the Rydberg frequency. The first and third are interpreted as resonance potentials of the M_3, M_4 series, the others as belonging to the M_5 series. The difference in ν/R for the two levels comes out 2.58. (2) *L series, 600 to 700 volts.* The three points observed correspond to Sommerfeld's L_ϵ, L_η and L_α, the ν/R values being 45.5, 47.0, and 51.5. These agree well with x-ray data.

Ionizing potentials for iron. The convergence limit of M_5 series is $\nu/R = 13.1$ which should correspond to an ionizing potential for that level. For the L series, the value for L_1 comes out $\nu/R = 59.0$.

Extreme ultra-violet spectrum of iron, 1188 to 18 A.—The critical potentials are interpreted as corresponding to emission lines of wave-length 264, 151, 129.6, 111.0, 94.6, 87.8, 83.9, 80.5 and 77.0 A. Differences between various pairs of the ν/R values correspond closely with eleven wave-lengths, from 294 to 1188 A, measured by Millikan, indicating that these belong to combination series. The L potentials correspond to 20.0, 19.4 and 17.7 A.

DURING the past two years a number of investigators have reported attempts to study the portion of the spectrum lying between the Millikan region and the x-rays by means of the photo-electric action of the radiation.[1-7] The general method used was to generate the radiation by electronic bombardment and study the total photo-electric effect as a function of the accelerating potential applied to the electrons producing the radiation. A discontinuity in the rate of increase of the photo-electric current was interpreted as indicating the excitation of characteristic radiation. In the earlier work this method gave only one

*DuPont Fellow in Chemistry 1922–23

[1] Richardson and Bazzoni, Phil. Mag. **42**, 1015 (1921)

[2] Kurth, Phys. Rev. **18**, 461 (1921)

[3] Hughes, Phil. Mag. **43**, (1922)

[4] Mohler and Foote, J. Wash. Acad. Sci. **11**, 273 (1921)

[5] Holweck, Ann. de Phys. (9) **17**, 5 (1922)

[6] Holtsmark, Phys. Z., **23**, 252 (1922)

[7] McLennan and Clark, Proc. Roy. Soc., A **102**, 389 (1923)

discontinuity for each spectral series in the region under investigation. These points have been interpreted as corresponding to the x-ray absorption limits, i.e., to the energy necessary to remove an electron from its normal position to infinity. Now in the ordinary x-ray region the absorption limits have been found to possess a fine structure on the high frequency side of the main absorption limit. The explanation which Kossel[8] has advanced for this is that the first absorption observed corresponds to the energy necessary to remove an electron from its normal energy level to the first incomplete electron shell and the other lines represent the energies necessary to eject the electron to the virtual orbits in the exterior of the atom. If this explanation is correct then a similar phenomenon should be observed in the soft x-ray region and therefore we should expect to find not one break in the photo-electric current but several for each x-ray series. This has now been observed, and this paper deals with the experimental procedure followed and the interpretation of the results.

Apparatus

The apparatus used is shown in Fig. 1. The radiation was generated by bombarding the solid target 1 with electrons from the hot tungsten filament 2, the accelerating potential being applied from the negative end of the filament to the target by means of a battery composed of small

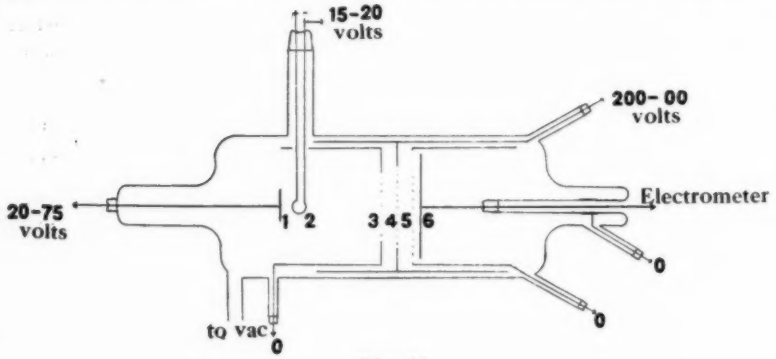

Fig. 1*

lead storage cells. The radiation fell upon the platinum plate 6 producing a photo-electric current which was measured by means of a Compton electrometer using the constant deflection method. The gauze 5 acted as a receiver for the photo-electrons. The gauze 4 was maintained at a potential at least 75 volts higher than 1 so as to keep positive ions from

[8] Kossel, Z. für Physik 1, 124 (1920)

* The potentials on *1* should read 20-750 volts and on 4 should read 200-1000 volts.

reaching the photo-electric plate. Gauze 3 was kept at a potential 15–20 volts lower than the negative and of the filament, thus stopping electrons. The gauzes 3 and 4 were constructed in such a manner that they shielded the parts of the tube around the photo-electric plate from the direct action of the radiation. It is to be noted also that the tube was constructed so that all the surfaces exposed to the action either of the direct radiation from the target or of that reflected from 6 were of metal and were maintained at definite potentials.

Before any measurements were made the tube was thoroughly evacuated by means of a mercury vapor pump backed up by an oil pump. During the evacuation the tube was heated to about 500°C and the target bombarded with electrons from the hot filament. The vacuum obtained in this way was such that during the experiments the pressure did not register on a McLeod gauge sensitive to a pressure of 10^{-5} mm. Mercury and other condensible vapors were frozen out in a liquid air trap. It was found impossible to obtain reproducible results if this high vacuum was not maintained.

As it is desirable to keep the initial conditions as nearly constant as possible the filament temperature was not changed during a run. The exciting current therefore, increased as the accelerating voltage was increased in the low voltage range. At high voltages a saturation current was obtained, so the exciting current was maintained at a constant value by slight alterations in the rheostat controlling the filament current whenever necessary. The electron current used ranged from 1 to 2.5 milli-amperes. This required a potential drop of 3–5 volts across the filament.

After running for some time it was found necessary to remove the target and free the surface from the tungsten which had been deposited. On replacing the target in the tube after such treatment and re-evacuating, the same breaks were always obtained.

Experimental Results

The method of experimentation was developed using an iron target. From the x-ray data on iron, it was estimated that some members of the M series should be found in the range of 50–100 volts. With this in view the region from 30–185 volts was studied first. The ratio of the photo-electric current to the exciting current was plotted along one axis and the accelerating voltage on the other. Fig. 2 shows one of the curves obtained. It is to be observed that the form of the curve is similar to that obtained by Franck and Einsporn[9] for mercury at lower voltages.

[9] Franck and Einsporn, Z. für Physik, **2**, 18 (1920)

The breaks, while small, are very definite and can be reproduced, although some of the fainter breaks do not appear in all the curves. Table I gives a complete list of the points obtained in this range. Curves 1–4 were run first, then the target was cleaned and the remaining curves

TABLE I

Critical points for iron at low voltages

Curve	1	2	3	4	5	6	7	8	9
1	47.2	82.5	96.4	.....	129.9	140.2	.....	.....	.....
2	46.9	.....	.....	111.7	.....	143.6	.....	152.0	.....
3	48.2	82.2	94.9	110.8	131.0	139.9	.....	153.7	.....
4	48.7	81.2	91.9	111.4	129.7	.....	.....	153.7	.....
5	45.7	83.0	96.3	112.0	.....	140.4	No readings above 155 volts		
6	46.2	80.5	94.1	112.0	.....	142.0	" "	"	" "
7	46.3	81.3	96.8	112.8	.....	.....	148.7	.....	160.5
8	46.2	82.2	95.4	110.2	.....	.....	146.2	.....	160.7
9	46.2	81.9	93.7	108.7	130.7	.....	146.4	.....	159.0
10	46.7	80.2	95.5	111.4	129.9	140.1	.....	153.7	.....
11	47.1	81.8	97.1	111.2	131.4	140.7	.....	153.9	.....
Av.	46.8	81.7	95.4	111.2	130.4	140.9	147.1	153.4	160.1
ν/R	3.46	6.03	7.05	8.21	9.63	10.40	10.88	11.33	11.83
λ	264	151	129.6	111.0	94.6	87.8	83.9	80.5	77.0

obtained. The values for the individual curves are given in volts; the values ν/R are the ratios of the frequencies to the Rydberg frequency; the wave-lengths λ are given in angstrom units. The relative intensities of the breaks are indicated fairly well by the number of times they were found.

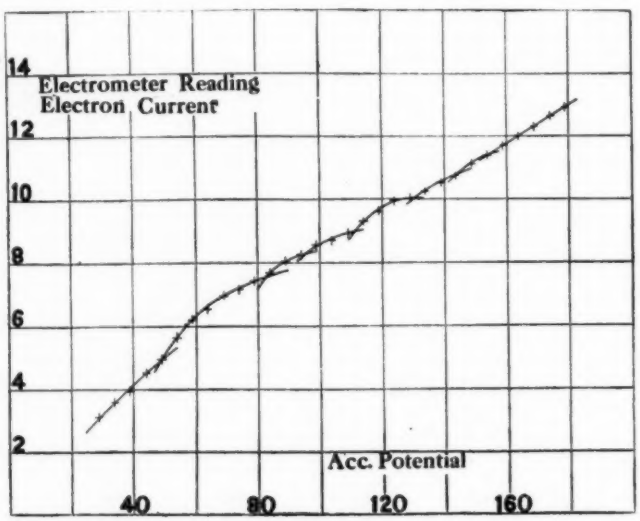

Fig. 2

A number of experiments were also carried on at higher and lower accelerating voltages. In the low voltage range the electrometer readings were too small to attain very high accuracy. The radiation was found to begin at 13–14 volts and rather definite breaks occurred at 20 and 26 volts. In this range readings were taken every two volts.

At high voltages some measurements have been made on the softer L lines. Readings were taken at ten volt intervals in this range so the values given are not as accurate as those for the M series. The breaks were found at 618, 637 and 697 volts; the corresponding wave lengths are 20.0, 19.4 and 17.7 angstrom units; the ν/R values are 45.5, 47.0 and 51.5.

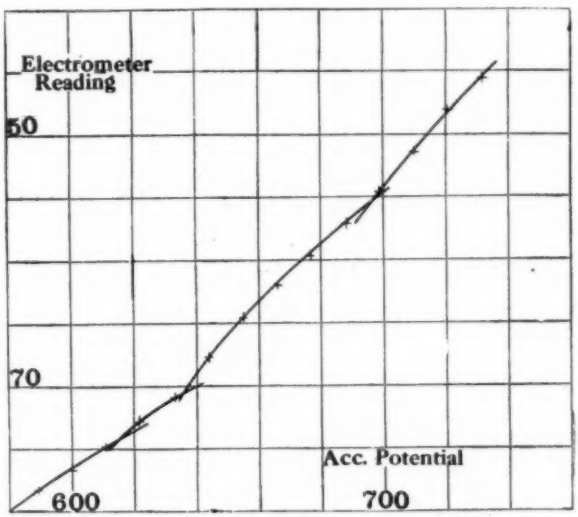

Fig. 3

One of the curves obtained is shown in Fig. 3. In this high voltage range the reason that only three lines were observed is probably because it was necessary to decrease the sensitivity of the electrometer considerably in order to handle the currents which were obtained; also, with the experimental arrangement used, it was necessary to take the points farther apart than at low voltages.

The experimental errors involved in making the measurements of the photo-electric and exciting currents were such that the points used in plotting the curves are accurate to about 0.5 per cent below 200 volts and 0.5 to 1 per cent in the higher range. In some runs, however, the readings were so large that the errors were even less. It is, therefore, evident that the breaks observed are considerably larger than the experimental errors.

Discussion of Results

The experimental procedure described in this paper is the same in principle as that employed by Franck and Einsporn[9] to study critical potentials in mercury vapor and by Olson and Glockler[10] to obtain the critical potentials in hydrogen. In their experiments gas molecules were bombarded with electrons, the radiation produced fell upon a metal plate and produced a photo-electric current which was measured by an electrometer. A sudden increase in the photo-electric current was found every time the energy of the bombarding electrons became great enough to remove an electron from its normal position in the atom or molecule struck to one of the orbits of higher quantic number. For example three of the critical potentials found by Franck and Einsporn for mercury correspond to the energy differences $1S-2P$, $1S-3P$, and $1S-4P$ (Sommerfeld notation) which had been determined previously from spectral data.[11] In my experiments a solid has been bombarded instead of a gas and higher voltages have been applied to the electrons. The critical potentials observed may be interpreted, by analogy to the above cases, as corresponding to differences between energy levels in the atom but these levels are so deep in the atom that the spectral lines corresponding to the same differences have not been observed up to the present time. It is possible however, to calculate some of these differences by applying the combination principle to the available x-ray data and thus test the interpretation given to the critical potentials.

Before proceeding with such calculations, the reasons will be given for interpreting the critical potentials reported in this paper as resonance potentials instead of following the policy of the earlier workers in this field who have classed all their values as ionizing potentials. The latter viewpoint is carried over from the x-ray theory which has interpreted the characteristic x-ray absorption limits as corresponding to the ionizing potentials of the various electron orbits within the atom. Some doubt has been cast upon the accuracy of this interpretation by the experiments of Stenstrom, Hertz, and Fricke on the M, L, and K limits respectively, who found a number of maxima in the absorption on the short wave-length side of the main absorption limit. In explanation of the maxima for the K-series—and a similar explanation can be given for the other series—Kossel suggested that "the principal limit corresponds to the energy which is necessary to remove an electron from the K shell to

[10] Olson and Glockler, Proc. Nat. Acad. 9, 122 (1923)

[11] For a more detailed discussion of the interpretation of critical potentials at low voltages the reader is referred to the third section of the sixth chapter in Sommerfeld's "Atombau und Spektrallinien" 3rd ed.

the periphery of the atom: the following maxima correspond to the transition of a K-electron to certain virtual quantic orbits which are distributed outside the atom."*

Carrying this viewpoint over into the soft x-ray region, the first critical potential for a given energy level should correspond to the removal of an electron from that level to the "periphery" of the atom. Whether this means to the outside of the valence shell, to the valence shell, or to one of the other shells which does not possess enough electrons to form a stable group of 4, 6, or 8 can not be determined from the x-ray measurements which have been made. We know from the work which has been done on resonance potentials that critical potentials are found corresponding to transitions in which the electron is transferred to one of the quantic orbits which lie beyond the valence shell, and from x-ray data we know that no such potentials are found corresponding to the transfer of an electron from an x-ray level to a completed shell of higher quantic number, but there is no theoretical or experimental basis for saying that such a transition can not terminate in one of the incomplete shells lying within the valence shell. In the following paragraphs we shall see that some of the critical potentials observed correspond to transitions of the latter type. The notation used in designating energy levels and in referring to spectral lines is the same as that used by Sommerfeld in the third edition of "Atombau und Spektrallinien." In general the critical potentials have been identified with emission lines although these lines have not been detected by ordinary spectroscopic methods; this practise, however, is in accord with that followed in the study of resonance potentials at low voltages in which case such a relationship has been found to exist.

The M-series of the heavy elements consists of five groups of lines, the classification being based on the M level into which the electron fal s. For elements of as low atomic number as that of iron, two pairs of the M levels are so close together in energy value that they can not be distinguished experimentally; hence the M-series appears to exist of only three groups of lines.[12] First, we have the lines due to the electrons falling into the M_1 and M_2 levels (in this discussion pairs of levels which differ only by the relativity separation will be considered as single levels since the separation for such elements as iron is too small to be detected in these experiments), then a higher frequency group corresponding to M_3 or M_4 as the final state, and finally a still higher frequency group

*The quotation is taken from Sommerfeld "Atombau and Spektrallinien" 3rd ed. p. 233.

[12] The evidence for this statement is given in an article by Bohr and Coster, Z. f. Physik **12**, 342 (1923).

corresponding to the transitions ending in M_5. From the known x-ray spectrum of iron we can calculate only one of the lines of the M_3-M_4 group. The Kβ line corresponds to the transition $M_3 \rightarrow K$ and the K_γ line to $N_5 \rightarrow K$ therefore the difference between the two corresponds to the transition from N_5-N_6 to M_3-M_4. The most recent values for the Kβ and K_γ lines are those given by Siegbahn,[13] the ν/R values (519.83 and 523.54) giving 3.71 for the difference. Older data give 519.55[14] and 523.1,[15] the difference being 3.55. Whichever value is used the agreement with the value 3.46 obtained for the first point in Table I is fairly good, especially since uncertain initial conditions make this point the least accurate. This point must therefore represent the first line of the M_3-M_4 group.

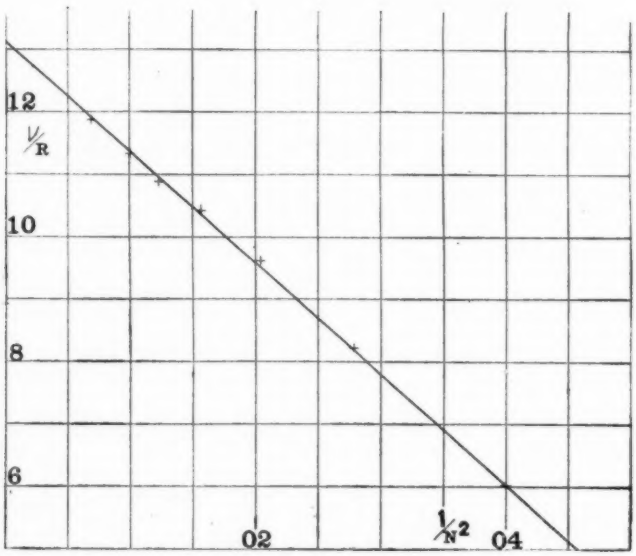

Fig. 4

In the iron atom we have electrons in the K, L and M levels and possibly one or two in the N but none farther out. It is to be expected, therefore, that the energies of the orbits of higher quantic number having the same azimuthal quantum number should be proportional to $1/N^2$ where N is the principal quantum number. The values of ν/R given in Table I were plotted against various values of $1/N^2$ to see if any such relationship could be found. On using 5, 6, 7, 8, 9, 10 and 12 for N it was found that the points numbered 2, 4, 5, 6, 7, 8, 9 in Table I would fall on a straight

[13] Siegbahn and Dolejsek, Z. f. Physik **10**, 159 (1922)
[14] Siegbahn, Ann. der Phys. **59**, 56 (1919)
[15] Siegbahn and Stenstrom, Phys. Z. **17**, pp. 48 and 318 (1916)

line as shown in Fig. 4, with an average deviation in terms of ν/R of .041, while omitting the point corresponding to $N=7$, the average deviation is .028. The points 1 and 3 are decidedly off this line and this is taken as an indication that they belong to another series. Now 1 has already been identified as corresponding to N_5-$N_6 \rightarrow M_3$-M_4 and therefore 1 and 3 are believed to be lines of the M_3-M_4 series and the others can be considered as the M_5 series, i.e. they correspond to transitions from levels having effective quantum numbers equal to the values used for N in the plot to the M_5 level.

The difference in the ν/R values of the points 1 and 2 is 2.57 and of 3 and 5 is 2.58; a point differing from 4 by a similar amount would fall too close to 2 to be detected with the apparatus used. This constant difference may be due to the fact that the points correspond to the ejection of electrons from the M_3-M_4 and M_5 levels to the same final levels. This may be tested by measurements on the L-series. The softest line in the L series corresponds to the transition from M_5 to L_1. From Siegbahn's[13] measurements on the K lines of iron we find the ν/R for Kα, corresponding to $L_1 \rightarrow K$ is 471.60 and for Kβ corresponding to $M_3 \rightarrow K$, is 519.83, giving a difference of 48.23 for $M_3 \rightarrow L_1$. The difference between M_3 and M_5 has been given above as 2.58. Subtracting this we obtain 45.65 for $M_5 \rightarrow L_1$. Experimentally, the first line of the L series was found at 45.5 which is a very satisfactory check and confirms the interpretation of the M lines. The points 1 and 3 in Table I are, therefore, the first and third lines of the M_3-M_4 series and the others are the M_5 series. The second line in the M_3-M_4 series falls too close to the first line of the M_5 series to be separated from that line with the apparatus used.

By extending the straight line shown in Fig. 4 the convergence limit of the M_5 series is found to be 13.1. From the known separation between the M_5 and M_3-M_4 levels we obtain 10.5 for the M_3-M_4 and combining the values for M_5 and $M_5 \rightarrow L_1$, 59.0 is obtained for L_1. These values differ considerably from those given by Sommerfeld[16] or by Bohr and Coster[17] but this is due to the values selected for reference levels by these authors. For the elements of atomic number 12 to 31 the K absorption limit has been chosen as the reference level. Now for the light elements Fricke[18] has shown that the K limit is not a single discontinuity in the absorption but consists of a number of such discontinuities, the first of which is the most pronounced, the others being less marked and finally merging into the continuous band. The first discontinuity is the one which has been

[16] Sommerfeld, Atombau und Spektrallinien, 3rd Edition, p. 630
[17] Bohr and Coster, Z. f. Physik **12**, 342 (1923)
[18] Fricke, Phys. Rev. **16**, 202 (1920)

used as the K limit. If Kossel's explanation[8] of this fine structure is correct then the value selected as the absorption limit does not correspond to the energy necessary to remove an electron from the K level to infinity but only to that necessary to take an electron from the K level to the "periphery" of the atom. The energy necessary for the ionization is represented more accurately by the beginning of the continuous band. The difference between these values as found by Fricke varies considerably with the different atoms, amounting to as much as 80 volts in some cases. This is of the same order of magnitude as the difference between the first line and convergence frequency of the M_5 series as given in this paper. Therefore, we may suppose that the values which have been derived in this paper are the true values for the removal of an electron to infinity.

The results may be further tested by applying the combination principle to calculate some lines in the Millikan region. The values given by Millikan[19] have been changed over to volts for convenience in comparison. They are given in the following table. The numbers in the column headed "combination" refer to the numbering of the points as given in Table I. No values lower than ten volts are given as at such voltages there are so many lines that the comparison has no significance.

TABLE II

Combination	G.K.R.	Millikan	Intensity
8–4	42.2	42.0	2
7–4	35.9	36.9	1
6–4	29.2	28.9	3
5–4	19.2	19.1	1
9–5	29.7	29.6	4
8–5	23.0	22.4	7
7–5	16.7	16.9	3
6–5	10.5	10.4	2
9–6	19.2	19.1	1
8–6	12.5	12.56	3
9–7	13.0	13.0	1
4–2	29.5	29.25	3

The three L lines which have been obtained are probably those corresponding to the transitions $M_5 \rightarrow L_1$, $M_5 \rightarrow L_2$, and $M_1 \rightarrow L_1$. The argument in favor of the first of these has been given in the discussion of the M lines. A similar calculation confirms the second line, as the only difference between the two is the difference between L_1 and L_2 which is known from the values of $K\alpha$ and $K\alpha'$. The observed and calculated values are 47.0 and 46.7 respectively. The third line is the $L\alpha$ line and this can be checked by extrapolating the Moseley curve for $L\alpha$. The extra-

[19] Millikan, Astrophysical J. **53**, 157 (1921)

polated value for $\sqrt{\nu/R}$ is 7.22 and the experimental value is 7.18, a very satisfactory agreement. According to the nomenclature used by Sommerfeld the lines are Lϵ, Lη and Lα respectively.

It is rather difficult to account for the failure of other investigators to obtain breaks such as those described in this paper since the information contained in the published reports is not sufficiently detailed. In some preliminary experiments with different tubes the writer found that one of the most important factors affecting the accurate measurement of the radiation effects was the control of the potential of every surface in the vicinity of the measuring plate. This is one thing which apparently has been neglected by most workers in this field as nearly all the published diagrams of apparatus show exposed glass surfaces near the photoelectric plate. Now under the conditions prevailing in an x-ray tube a glass surface cannot be said to be at a known or even constant potential and variations in the potential of such surfaces will materially affect the accuracy of the work. Another factor which must be considered is the potential drop across the filament, which must be small.

Summary

It has been found that spectral lines can be detected in the soft x-ray region by studying the total photo-electric effect produced by the radiation as a function of the accelerating voltage applied to the electrons producing the radiation. This method has been used to measure the wave-lengths of nine M lines of iron between $\lambda = 264$A and $\lambda = 77$A, and three L lines $\lambda = 20.0$, 19.4 and 17.7A. These measurements show that the method is capable of filling in the gap in the spectrum between the ultra-violet and the x-ray regions. By applying the combination principle it has been shown that the results obtained are in accord with Millikan's measurements in the extreme ultra-violet spectrum of iron and also with Siegbahn's measurements on the K-series of iron.

In conclusion the writer wishes to express his thanks to Professor G. N. Lewis for the aid and encouragement he has extended during the progress of this research.

Department of Chemistry,
University of California,
May 20, 1923.

ABSORPTION OF POTASSIUM VAPOR AT HIGH TEMPERATURES, AND SATELLITES ACCOMPANYING THE MEMBERS OF THE PRINCIPAL SERIES

By A. L. Narayan and D. Gunnayya

Abstract

Absorption spectrum of potassium vapor at high temperatures.—Further experiments have confirmed the existence of the lines λλ5340, 5300, 5205, 5100, 4970, and 4831 previously noticed. The line 4831 was well defined and in intensity comes next to 4641 and 4642; it probably is the combination line ($1P-8D$). The line 4120 was obtained distinctly reversed. The absorption spectrum showed among other lines some 15 *satellites* accompanying P_3 to P_8, which are not found in the emission spectrum. They increase in number and in width as vapor density is increased, finally coalescing to form a wide band.

IN THE course of our recent experiments on the absorption of the vapor at different temperatures,[1] it was found that the vapor showed traces of absorption in the associated series, some of which seemed to correspond to $1P-mD$. Experiments subsequently conducted in the laboratory not only confirmed the existence of these lines but also of the line 4831 which when observed in the previous experiments at high temperatures was found to be in intensity next to 4641–4642. As a result of attempts to correlate this line, the authors believe that this is the combination line $1P-8D$, the observed and calculated wave-numbers being 20699.5 and 20694.3 (21963.06–1268.8); and it is very significant that one of its terms is $1P$ as it appears only at high temperatures along with $1P-mD$ lines. This line is undoubtedly the same as the emission line observed by Robertson in his experiments on electrodeless discharge in potassium vapor.[2]

It is possible that the valence electron is first thrown in this case by thermal agency, out of the fundamental orbit into the $1P$ orbit further removed from the nucleus. Isolated lines of this type were observed by Lenard for the alkali metals.

Furthermore, the line 4120 observed by Datta in Rayleigh's vacuum arc lamp as a faint line, has been obtained distinctly reversed.

[1] Narayan and Gunnayya, Nature Aug. 1922, Astrophysical J. Apr. 1923 and Phil. Mag. May, 1923

[2] Robertson, Phys. Rev. **19**, 470, May, 1922

In these experiments, besides the lines of the principal series, new lines which do not correspond to the emission lines of K were observed at high temperatures. These new lines which are simply satellites clustered together within a small compass about the principal line, which is the strongest of the assemblage, become with the increase of vapor density larger in number and more diffuse until at last they coalesce together with the principal line to form a wide band. By gradually increasing the density of the vapor and by photographing the absorption spectrum[3] at different stages, it is possible to recognise these lines. The wave-lengths along with their wave-numbers are given in the following table:—

	Line	*Satellites*	*Wave number*
P_3	4047.2	4119.1*	24280
	4044.55	4025.3	24849
		3434.6	29114
P_4	3446.72	3461.65	28883
	3447.7	3468.45*	28830
		3482.15*	28719
		3221.6	31044
P_5	3217.66	3223.36	31027
	3217.17	3214.00	31100
P_6	3102.0	3100.00	32250
	3101.8	3103.5	32225
P_7	3034	3033.15	32967
		3036.55*	32925
P_8	2992.2	2990.34	33436
		2994.05*	33391

Experiments are now in progress to study the absorption and emission of this vapor when it is excited by the purely optical method developed by Füchtbauer for Hg vapor.[4]

M. R. COLLEGE,
VIZIANAGARUM, INDIA,
July 7, 1923.

[3] See Phil. Mag. (6) **45**, Pl. XII, Fig. 1, May, 1923

[4] Füchtbauer, Phys. Z. **21**, 635, 638, Nov. 1 and 15, 1920

*Not recorded by Datta who observed a similar phenomenon, (Proc. Roy. Soc. A **101**, p. 539) which was probably due to the comparatively low density of the vapor in his experiments. A careful examination shows that the main line is split into two.

THE NEAR INFRA-RED ABSORPTION SPECTRA OF SOME ORGANIC LIQUIDS

By Joseph W. Ellis

Abstract

Near infra-red absorption spectra of thirty-one organic liquids to 2.5μ.—*A self-recording prism spectrograph*, Littrow mounting, with dispersion equivalent to two 60° flint glass prisms—considerably greater than had hitherto been used in this region—was arranged so that the spot of light from the mirror of the galvanometer in the thermopile circuit, was focused on a sheet of bromide paper on a drum rotated in gear with the prism table. Curves thus obtained are reproduced which show the transmission through 11 mm of certain organic liquids: *ethyl, methyl, propyl, butyl, ethylene and methylene halides, butyl nitrite, benzene, toluene, pentane, hexane, heptane, octane, mesitylene, paraxylene, chloroform and bromoform.* In a table are given the wave-lengths of the absorption maxima accurate to about .01μ, and, in many cases, the percentage absorption, accurate to five per cent. Curves obtained by visual observations, are also given for eight of the above compounds and for *acetone and ethyl ether.* Bands near 0.90, 1.02, 1.17, 1.38 and 1.70μ occur in most if not all of these spectra. Hence these *bands are attributed to the C-H bond*, and appear to be, respectively the 7th, 6th, 5th, 4th, and 3rd harmonics of a fundamental frequency found by Coblentz at 6.9μ. There are also bands at 1.81, 1.91, 2.00 and 2.10μ which occur for several liquids. Shifts in the positions of the bands for different liquids, which may amount to $\pm$ .03μ, are not understood, but may be due to a change in the relation intensity of the two components of the band; for some of the bands are clearly double, like the infra-red bands due to gaseous compounds. The simple quantum theory of such gaseous spectra does not seem to hold directly for these liquid spectra, however, since the separation of the components of 1.38μ and also of 1.7μ is greater for the iodides than for the corresponding chlorides.

Introduction

WHILE rock salt has proved to be the best prism material when investigations into the far infra-red region of the spectrum are desired, since it transmits as far as about 15μ, in studying the near infra-red region, prisms with a higher dispersive power, such as quartz, glass or carbon bisulfide may be used.[1] Puccianti,[2] using a single quartz prism, studied fifteen carbon compounds in this region and found that all the compounds in which there is a direct linkage of carbon and hydrogen have an absorption band at 1.71μ. Besides making investigations with a rock salt prism, Coblentz[3] studied the absorption of over

[1] The relative dispersive powers of rock salt, quartz, fluorite and carbon bisulfide are given in Scientific Papers Bur. Stand. No. 401, 1920.

[2] Puccianti, Nuovo Cim., **11**, 141, 1900; Phys. Zeit. 1899–1900.

[3] W. W. Coblentz, Astrophys. J. **20**, 1904

twenty compounds in the region between the visible and 2.7μ with a quartz spectrograph. He also found the 1.71μ band wherever there was a C-H linkage. In all this work use was made of the heating effect of the infra-red rays falling on a bolometer, thermopile or radiometer. Abney and Festing,[4] the first investigators of infra-red absorption spectra, alone seem to have used a photographic method. They were able to produce a photographic plate sensitive to light of wave-lengths as great as 1.2μ. Their work shows a large number of absorption bands and lines up to this wave-length limit.

It was felt that an investigation in the near infra-red would yield valuable data provided a comparatively high dispersion could be obtained; consequently, a spectrograph with rather dense flint glass prisms was assembled. With the use of this instrument many organic compounds have been studied whose infra-red absorption spectra have heretofore been examined, if at all, only with the use of rock salt prisms; and as a result many absorption bands have been obtained which never could be resolved with such prisms.

Apparatus and Calibration

A brief discussion of the work begun and a brief description of the spectrograph used have already been given.[5] Since the publication of that article an automatic method has been adopted for the recording of the absorption curves. A diagram of this improved apparatus is given in Fig. 1. The source of radiation S was a 108-watt lamp, intended for a

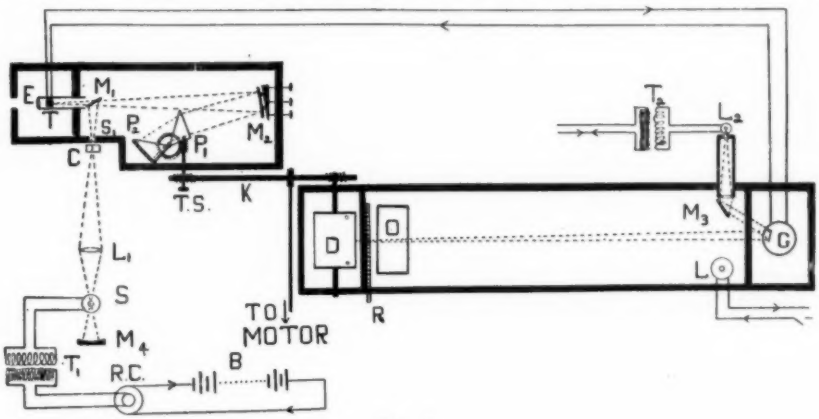

Fig. 1

locomotive head-light, operating on six volts A.C. To insure a steady source, it was operated on a current supplied by a storage battery B,

[4] Abney and Festing, Phil. Trans. **172**, 1881

[5] J. W. Ellis, Science, **54**, Sept. 15, 1922

after it had been properly converted and stepped down to the proper voltage by the rotary converter RC and the transformer T_1. By placing the concave mirror M_4 behind the source, about 40 per cent increase in transmission was obtained.

A small quartz lens L_1 focused the light upon the slit S_1 through a glass absorption cell C. After reflection from the plane speculum mirror M_1 and the concave speculum mirror M_2 the light entered the glass prism P_1. The back surface of the prism P_2 was silvered; so for any given position of P_2 only a small portion of the spectrum struck this silvered surface normally, and retraced its path to M_2 and then to the thermopile T. M_2 was slightly tilted so that this light on second reflection passed over M_1. The thermopile was of the Hilger type with ten bismuth-silver couples. E represents an eye-piece for the direct observation of visible light. The sensitive Leeds-Northrup galvanometer G used with the thermopile was placed on an isolated support to eliminate mechanical jarring.

The self-recording device consisted partly of a cylindrical drum D, 13 cm long and 48 cm in circumference, geared directly to the screw that also rotated P_2, by means of the shaft K. The thumbscrew TS enabled the gear at P_2 to be released at any time and P_2 brought back to its zero position. The gear ratios were so chosen that when P_2 had caused the region of the spectrum between 0.589μ and 2.7μ to pass before the thermopile, D had made one complete revolution. The shaft was driven by means of a slowed-down motor system so that it required fifteen minutes for one revolution of D. A strip of sensitized double-weight photographic paper was securely clamped around the drum. The light from the lamp L_2 was reflected from M_3 and the galvanometer mirror, and the magnified image of a single filament of L_2 was brought to a focus upon the screen in front of the drum. This screen was traversed by a narrow horizontal slit parallel to the axis of D, so that the intersection of the vertical image of the filament with this slit formed a spot of light on the photographic paper. The combination of the rotational motion of D and the horizontal motion of the image of the filament, caused by the swinging of the galvanometer mirror, traced a curve representing the absorption spectrum of the substance in C.

When a curve was to be taken, P_2 was set so that the D-lines of sodium fell upon the thermopile. The shutter R was then removed, and a lamp L within the dark box was thrown on for about a second, so as to give a dark line on the photographic paper which was taken as the zero line in all this work. A window of red glass O was used for observing the position of the image of the filament at any time. This was necessary because of the progressive shift of the galvanometer mirror at times.

The average dispersion obtained by means of these two 30° flint glass prisms, since the light traversed each prism twice, was between two and three times that obtained with a single 60° quartz prism, and between four and five times that obtained with a single 60° rock salt prism, considerably greater than that previously used in similar experiments.

The instrument was calibrated twice, both before and after the substitution of the self-recording device. The former calibration was more easily accomplished as the observing telescope was 2.5 meters distant from *G* while the distance *DG* was only one meter. Certain emission lines of lithium, sodium, thalium, strontium, and calcium, obtained by the use of cored carbons in a direct current arc, and several solar absorption bands were used for calibration. The greatest emission wave-lengths observed were at 1.85μ in sodium and 1.98μ in calcium. In the second calibration use was also made of the sharp absorption maxima in the spectrum of chloroform observed by the visual method.[6]

Results and Discussion

Visual method. Twelve substances were studied by means of the visual method. The absorption curves of ten of these are given in Fig. 2. Percentage transmission is plotted against wave-length in microns. A differential method was used; observations were made for a given setting of the prism, first with an empty cell and then with a 3 mm cell of the substance. Because of decreased internal reflection with a filled cell the ratio of the deflections observed with the cell filled and with the cell empty, was greater than unity in regions of apparently perfect transmission. Corrections were made throughout, therefore, on the assumption that these were regions of one hundred per cent transmission.

These ten curves are strikingly similar in that they all have three absorption bands in common in the neighborhood of 1.17μ, 1.38μ, and 1.7μ. The band at 1.7μ, as was pointed out by Puccianti[2] and Coblentz,[3] is characteristic of all carbon-hydrogen compounds examined by them. There are shifts in the positions of these common absorption bands, however, which are greater than the limit of experimental error, but the slight irregularities in the region 0.8μ to 1.0μ are due largely to experimental errors, as the absolute deflections here were much smaller than at 1.5μ.

Self-recording method. Some thirty substances have been examined with the self-recording photographic device. These included chloroform, bromoform, certain ethyl, methyl, propyl, butyl, ethylene and methylene halides, as well as some simple hydro-carbons, such as benzene, toluene,

[6] J. W. Ellis, Phys. Rev. **19**, May, 1922

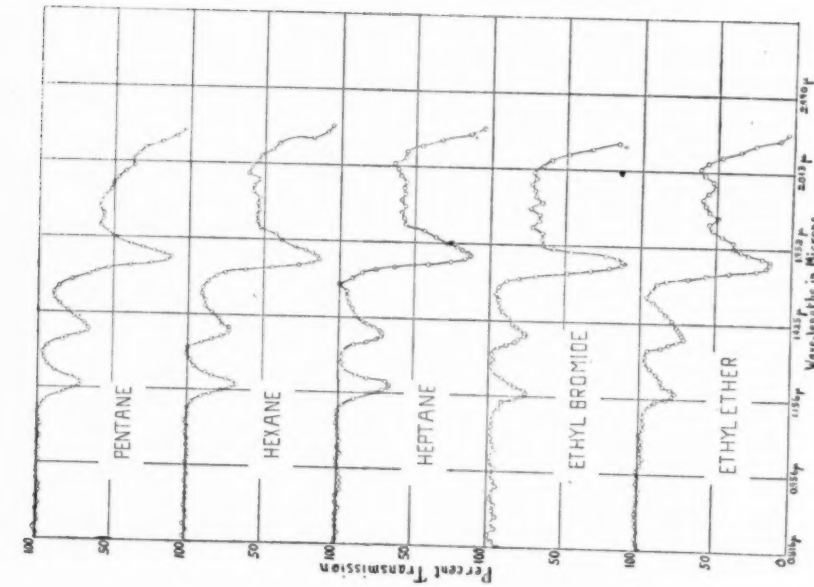
PENTANE
HEXANE
HEPTANE
ETHYL BROMIDE
ETHYL ETHER
Per cent Transmission
Wave-lengths in Microns.

Fig. 2b

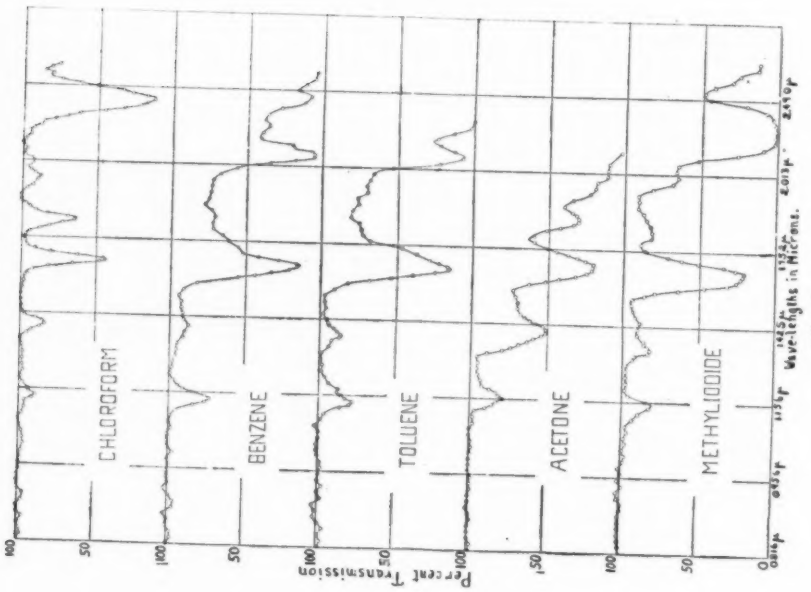
CHLOROFORM
BENZENE
TOLUENE
ACETONE
METHYLIODIDE
Per cent Transmission
Wave-lengths in Microns.

Fig. 2a

pentane, hexane, etc. Unless otherwise specified these compounds are the normal compounds. The thickness of the cell was 11 mm, or slightly more. The absorption curves, many times reduced, for most of the compounds are given in Figs. 3 and 4. The original records were 10 by 48 cm. The plain intensity distribution curve is shown in Fig. 3a. The regions of selective absorption in it are probably due to water vapor in the atmosphere.

Striking similarities among these spectra are evident. Besides the bands common to all in the neighborhood of 1.17μ, 1.38μ, and 1.7μ, in many of the compounds bands near 0.9μ and 1.0μ appear. The wave-lengths of the various maxima are recorded in Table I. In this table is also included the percentage absorption wherever its approximate measurement was found practicable. This was done by sketching the original intensity curve upon the spectrum curve, and taking the ratios of ordinates at the points of interest. The fair degree of consistency obtained in this manner indicates an average error of less than five per cent. The depth of these bands, however, is affected by the proximity of other bands and their lack of resolution.

In locating the positions of the absorption maxima, the intersection of a line drawn tangent to the absorption curve and having the slope of the original intensity distribution curve at that wave-length was taken as the minimum point of the curve. In the case, however, of the broad bands at 1.7μ, approximately the center of each band was chosen for the absorption maxima.

At least two curves were taken for nearly every substance. The details of the curves, such as points of inflection in the case of the resolution of two bands, were duplicated in almost every instance.

As carbon and hydrogen are the only elements which these substances have in common we must attribute these bands to them. Coblentz[7] studied the near infra-red absorption spectra of several vegetable and animal oils, and has found that they all have bands near 1.17μ, 1.39μ, and 1.75μ. Examination of the curves shows most of them to have selective absorption near 0.9μ and 1.0μ. Now it has been pointed out by other investigators and verified in this research, that substances such as CS_2 and CCl_4, which have carbon without hydrogen, have no absorption bands in this region. Compounds which have the hydrogen without the carbon do not show these bands. Consequently, we have to ascribe their presence to the C-H linkage in the compound. Although a quantitative comparison of the depths of these common bands among different sub-

[7] W. W. Coblentz, Scientific Papers Bur. Stand., No. 418, 1921

stances would have to take into consideration the molecular concentration, one can see in a general way that the depth of the band is a direct function of the number of C-H groups in the molecule.

It is very apparent that the halogen in the aliphatic halides studied plays but a very small part in the selective absorption in this region. It would seem, however, that we should ascribe the progressive separation, or resolution, of the double band at 1.38μ in the case of the ethyl halides, Fig. 3a, and of the methylene halides, Fig. 4a, to the halogen. The order of these separations is also the order of the atomic weights of the halogen: chlorine, bromine, iodine. This band has a wide separation for methyl iodide also, but unfortunately methyl chloride and methyl bromide are gases at ordinary temperatures, and were not studied.

TABLE I

Near infra-red absorption maxima for some organic liquids to 2.4μ.
Wave-length in μ; per cent absorption of 11 mm cell in brackets.
Values obtained by Puccianti, Iklé or Coblentz indicated thus (1.15P) etc.

Ethyl chloride C_2H_5Cl	.905	1.02	1.175(58)	1.37 (58)	1.70 (96)
Ethyl bromide C_2H_5Br	.90	1.01	1.165(54)	1.365(52)	1.69 (96)
Ethyl iodide C_2H_5I	.90	1.015	1.17 (54)	1.37(47)	1.70 (94)
	(.83P)	(.96P)	(1.15P)	(1.40P)	(1.72P)
Methyl iodide CH_3I	.895		1.15	1.35 (45)	1.66 (29)
	(.89P)		(1.15P)	(1.39P)	(1.70P)
Propyl bromide $CH_3{\cdot}CH_2{\cdot}CH_2Br$	.905	1.015	1.175(56)	1.365(53)	1.70 (96)
Propyl iodide $CH_3{\cdot}CH_2{\cdot}CH_2I$	.905		1.75 (57)	1.365(51)	1.69 (97)
Iso-propyl iodide $(CH_3)_2{\cdot}CHI$	.915		1.175(59)	1.365(50)	1.70 (97)
Butyl chloride $CH_3{\cdot}(CH_2)_2{\cdot}CH_2Cl$	.925		1.18 (59)	1.375(58)	1.70 (95)
Iso-Butyl chloride $(CH_3)_2{\cdot}CH{\cdot}CH_2Cl$	.915		1.175(56)	1.37 (63)	1.70 (96)
Butyl bromide $CH_3{\cdot}(CH_2)_2{\cdot}CH_2Br$	.915	1.025	1.18 (60)	1.37 (56)	1.70 (97)
Iso-Butyl bromide $(CH_3)_2{\cdot}CH{\cdot}CH_2Br$	.915		1.175(58)	1.365(56)	1.70 (96)
Butyl iodide $CH_3{\cdot}(CH_2)_2{\cdot}CH_2I$	.920		1.18 (59)	1.37 (55)	1.705(95)
Iso-Butyl iodide $(CH_3)_2{\cdot}CH{\cdot}CH_2I$	.915		1.175(53)	1.37 (48)	1.70 (95)
Butyl nitrite $(CH_3{\cdot}(CH_2)_3\ CH_2NO_2$	.920		1.185(56)	1.37 (54)	1.705(97)
Butyl ether $(C_4H_9)_2O$	.920		1.19 (64)	1.375(67)	1.70 (98)
Pentane $CH_3(CH_2)_3CH_3$	.915	1.015	1.185(56)	1.375(54)	1.705(94)
Hexane $CH_3(CH_2)_4\ CH_3$	.925	1.03	1.195(70)	1.38 (63)	1.72 (96)
Heptane $CH_3(CH_2)_5\ CH_3$	.925	1.035	1.19 (67)	1.38 (60)	1.72 (92)
Octane $CH_3(CH_2)_6\ CH_3$	.930	1.035	1.195(66)	1.385(60)	1.72 (94)
Mesitylene $(C_6H_3)_3$	.915	1.015	1.18 (54)	1.37 (56)	1.705(94)
Methylene chloride CH_2Cl_2	.890, .935	1.03	1.15 (36)	1.39 (41)	1.675(92)
Methylene bromide $CH_2\ Br_2$	.890	1.035	1.15 (38)	1.365(32)	1.68 (90)
Methylene iodide CH_2I_2	.895	1.03	1.15 (28)	1.37 (26)	1.68 (18)
Chloroform $CHCl_3$	.890	1.015	1.145(19)	1.385(36)	1.66 (65)
	(.84C)	(.99C)	(1.12, 1.21C)		(1.671, 1.71C)
Bromoform $CHBr_3$	.89	1.015	1.15 (23)	1.40 (57)	1.67 (74)
Ethylene bromide $C_2H_4Br_2$	.895		1.16 (42)	1.38 (39)	1.685(95)
Ethylene chloride $C_2H_4Cl_2$	.90		1.16 (46)	1.39 (47)	1.685(91)
Benzene C_6H_6	.885	(.99P)	1.145(51)	1.39 (22)	1.66 (93)
	(.86P)	(1.02C)	(1.13P)	(1.43C)	(1.68P)
Toluene $C_6H_5CH_3$	.885-.915		1.145(48)	1.375(37)	1.70 (93)
	(.87P)	(1.03P)	(1.16P)	(1.44P)	(1.70P, 1.71C)
Para-xylene $C_6H_4\ (CH_3)_2$	.895-.915	1.02	1.155(46)	1.38(48)	1.705(94)
	(.86P)	(.94P)	(1.22P)	(1.41P)	(1.71PC)
Cotton-seed oil	.93	1.04	1.195(70)	1.395(70)	1.73 (95)
			(1.18C)	(1.39C)	(1.75C)

TABLE I (*Continued*). Additional absorption maxima

Ethyl chloride C_2H_5Cl		1.81 (70)	1.90(40)	1.995(45)	2.085(33)	
Ethyl bromide C_2H_5Br		1.815(63)	1.90(51)	2.00(53)		
Ethyl iodide C_2H_5I		1.84(50)	1.93(45)	2.04(42)		
		(1.85P)				(2.3P)
Methyl iodide CH_3I	1.45(42)	1.86(32)			2.10(54)	
	(1.49P)	(1.85P)			(2.13P)	(2.37P)
Propyl bromide $CH_3{\cdot}CH_2{\cdot}CH_2Br$			1.90(70)			
Propyl iodide $CH_3{\cdot}CH_2{\cdot}CH_2I$			1.90(64)	2.005(53)		
iso-propyl iodide $(CH_3)_2{\cdot}CHI$			1.90(55)	1.985(53)		
Butyl bromide $CH_3{\cdot}(CH_2)_2{\cdot}CH_2C_1$				1.99(64)		
Iso-butyl bromide $(CH_3)_2CH{\cdot}CH_2C_1$			1.90(68)	1.985(57)		
Pentane $CH_3(CH_2)_3\,CH_3$		1.82	1.90			
Hexane $CH_3(CH_2)_4\,CH_3$		1.81(90)				2.42
Heptane $CH_3(CH_2)_5\,CH_3$		1.80(88)				
Octane $CH_3(CH_2)_6\,CH_3$		1.80(91)				(2.38C)
Mesitylene $(C_6H_3)\,(CH_3)_3$		1.86(60)	(1.95C)	2.025(61)	(2.2C)	(2.3C)
Methylene chloride $CH_2\,Cl_2$		1.86(49)	1.98(20)	2.095(29)		
Methylene bromide $CH_2\,Br_2$	1.405(40)	1.875(47)	1.925(38)	2.045(23)		
Methylene iodide CH_2I_2	1.425(34)	1.835(32)	1.94(24)	2.07(47)	2.14	
Chloroform $CHCl_3$	1.50(12)	1.835(56)	(1.916I)	2.105(20)		2.425(2.38C)
Bromoform $CHBr_3$	1.535(30)	1.89(60)	(1.92I)	2.07(65)		
Ethylene bromide $C_2H_4Br_2$		1.86(58)		2.01(35)		
Ethylene chloride $C_2H_4Cl_2$		1.86(57)		2.01(35)		
Benzene C_6H_6	1.73, 1.79	1.85(47)	1.90(38)		2.18(95)	
			(1.95P)	(2.05P)	(2.18CP)	
Toluene $C_6H_5CH_3$		1.86(48)		2.02(50)	(2.18P)	(2.34P)
Para-xylene $C_6H_4\,(CH_3)_2$		1.86(53)		2.025(53)		
		(1.84P)		(2.06P)	(2.18P)	(2.34P)

It seems quite probable that the 1.7μ band for at least most of the compounds is not a single band. In many cases at least two distinct bands are seen, and the breadth of others would indicate a combination of two or more bands. This band seems to be triple in the case of methylene iodide and also perhaps in the cases of methylene chloride and, bromide. Comparison with the results of the visual observations and also of the curves for toluene, pentane, hexane and heptane shows there is a tendency for the minima to be displaced toward a longer wave-length in many substances when a thicker cell is used. Since absorption follows a logarithmic law, we should expect such a shift only when the longer wave-length component of a double band is more intense.

The spectra of chloroform and bromoform, Fig. 4a, are very similar. However, there is a shift toward the longer wave-lengths in the case of bromoform. These two compounds have the best defined bands of all the substances examined. They are also the most transparent. This fact is in accordance with the observation made by Iklé[8] that the presence of a greater amount of any halogen in a compound increases its diathermancy.

In Figs. 3b and 3c are given the curves of the propyl and of the butyl compounds. No appreciable differences are observed between the normal

[8] Max Iklé, Dissertation, Berlin, 1903

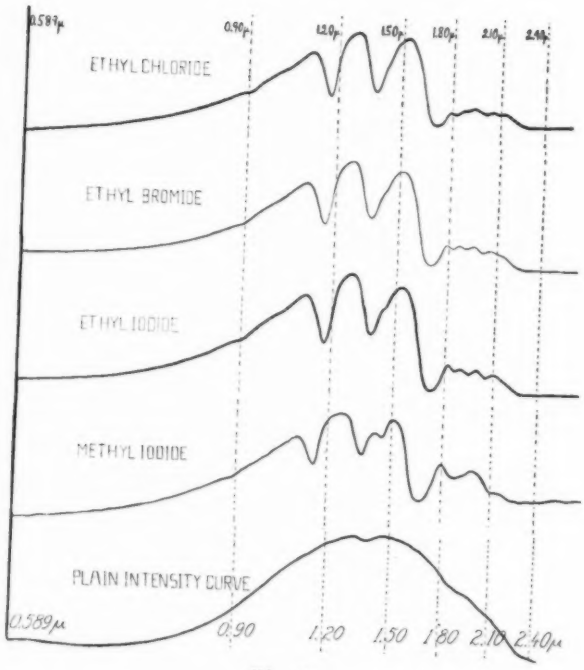
0.589μ
0.90μ
1.20μ
1.50μ
1.80μ
2.10μ
2.40μ
ETHYL CHLORIDE
ETHYL BROMIDE
ETHYL IODIDE
METHYL IODIDE
PLAIN INTENSITY CURVE
0.589μ
0.90
1.20
1.50
1.80
2.10
2.40μ

Fig. 3a

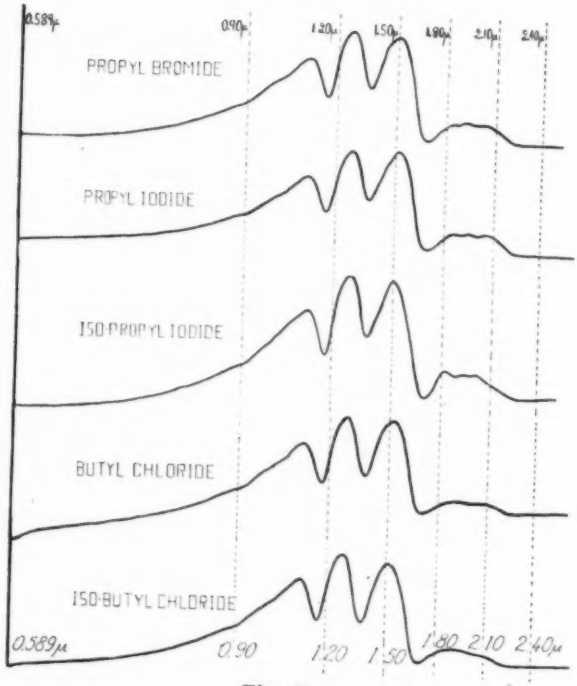
0.589μ
0.90μ
1.20μ
1.50μ
1.80μ
2.10μ
2.40μ
PROPYL BROMIDE
PROPYL IODIDE
ISO-PROPYL IODIDE
BUTYL CHLORIDE
ISO-BUTYL CHLORIDE
0.589μ
0.90
1.20
1.50
1.80
2.10
2.40μ

Fig. 3b

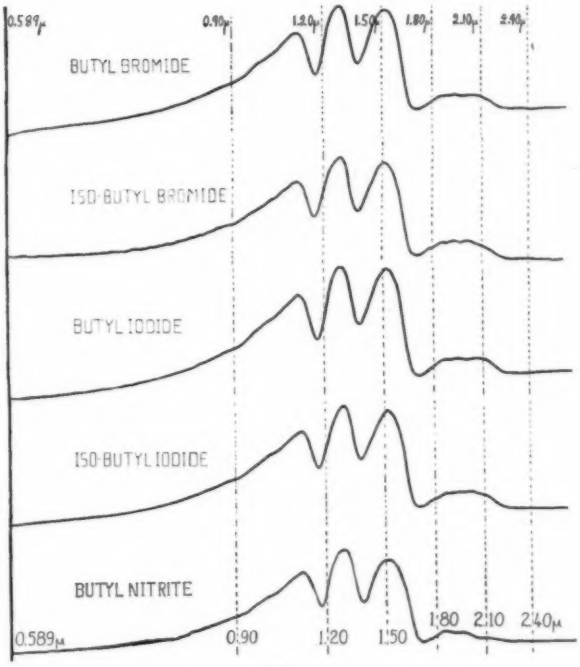
BUTYL BROMIDE
ISO-BUTYL BROMIDE
BUTYL IODIDE
ISO-BUTYL IODIDE
BUTYL NITRITE
0.589μ
0.90
1.20
1.50
1.80
2.10
2.40μ

Fig. 3c

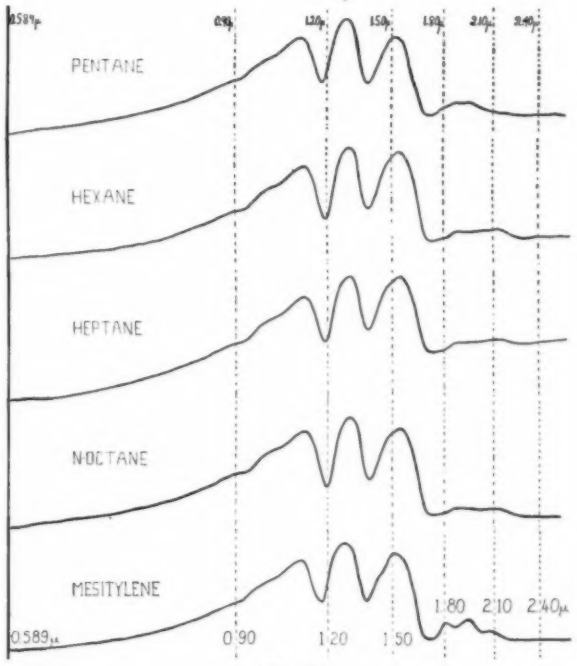
PENTANE
HEXANE
HEPTANE
N-OCTANE
MESITYLENE
0.589μ
0.90
1.20
1.50
1.80
2.10
2.40μ

Fig. 3d

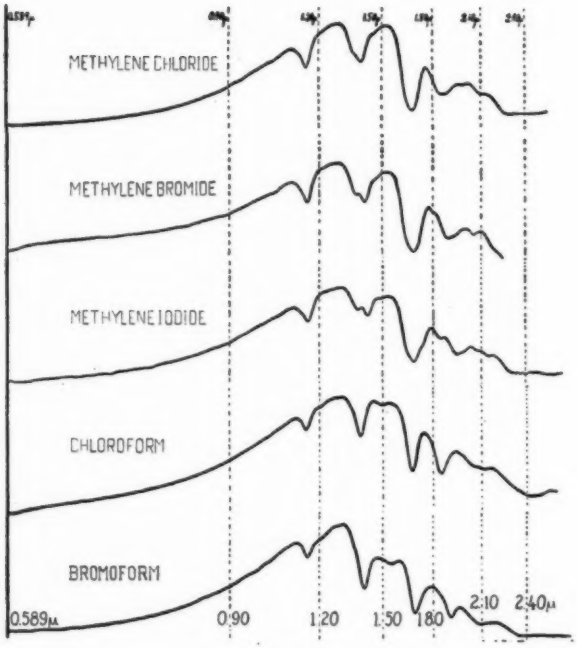
METHYLENE CHLORIDE
METHYLENE BROMIDE
METHYLENE IODIDE
CHLOROFORM
BROMOFORM
0·589μ
0·90
1·20
1·50
1·80
2·10
2·40μ

Fig. 4a

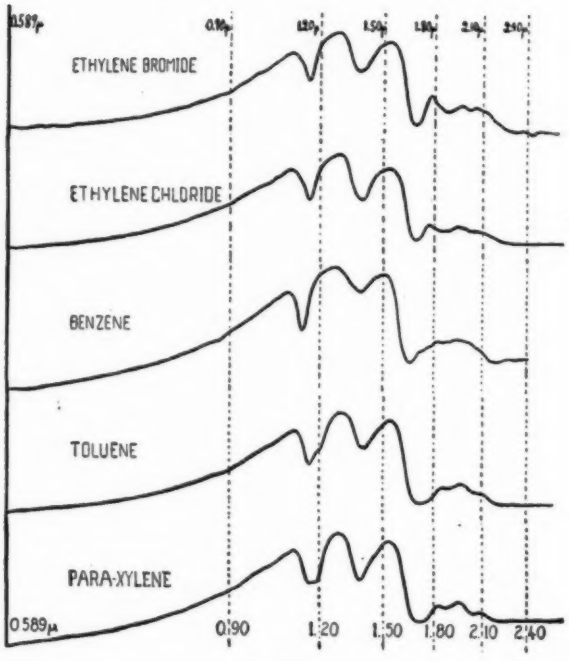
ETHYLENE BROMIDE
ETHYLENE CHLORIDE
BENZENE
TOLUENE
PARA-XYLENE
0·589μ
0·90
1·20
1·50
1·80
2·10
2·40

Fig. 4b

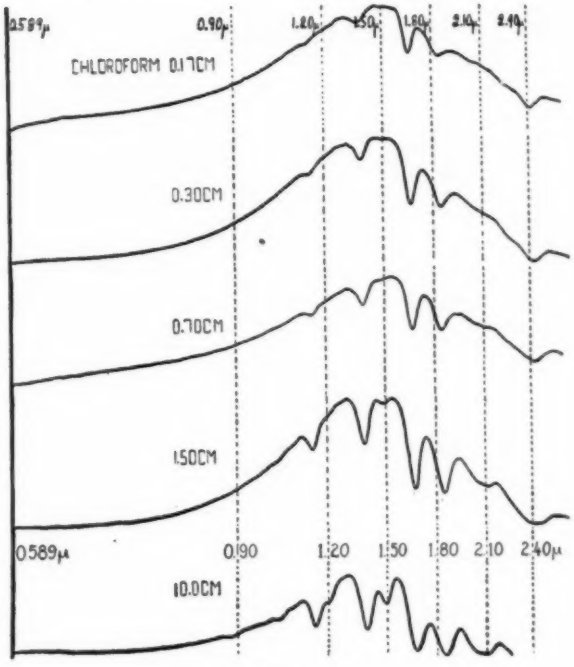
CHLOROFORM 0.17CM
0.30CM
0.70CM
1.50CM
10.0CM
0.589μ
0.90
1.20
1.50
1.80
2.10
2.40μ

Fig. 4c

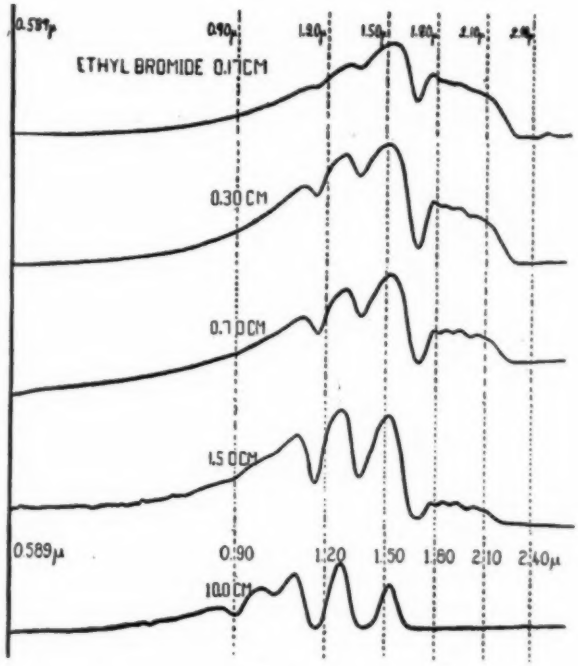
ETHYL BROMIDE 0.17CM
0.30 CM
0.70CM
1.50CM
10.0CM
0.589μ
0.90
1.20
1.50
1.80
2.10
2.40μ

Fig. 4d

and the iso- compounds; nor between the curve for butyl nitrite and those for the butyl halides.

The effect of the change of thickness of the cell upon the form of the curves is well shown for chloroform and ethyl bromide in Figs. 4c and 4d. Thicknesses varying from 0.17 cm to 10.0 cm were used for each. Sin ce the bands at 0.9μ and 1.0μ show plainly for the 10 cm cells, although th ey were entirely obscured for the 1.1 cm cell for chloroform, the probabil ty that these two bands are also common to all C-H compounds is increased.

The spectrum of cotton-seed oil also was taken. Its absorption maxima are tabulated in Table I and agree well with those given by Coblentz.[7]

Correction to Puccianti's values. More accurate determinations of the indices of refraction for quartz for infra-red light have been made since Puccianti[2] made his investigations. Fortunately, he recorded the refracting angle of his prism and also the deviation for several absorption bands. When the new values of these indices of refraction as given by the Bureau of Standards[1] are applied, somewhat different values from those computed by Puccianti are obtained (see Table II).

TABLE II

Corrections to Puccianti's values

Puccianti's values	Corrected values	Difference
1.150μ	1.146μ	0.004μ
1.440	1.388	0.052
1.710	1.690	0.020
2.180	2.156	0.024

The corrected values agree more closely with those of the present investigation.

The duplicity of the bands. It is a well known theory that absorption bands in the near infra-red spectra of gases should not be single but rather triple bands, the center corresponding to an oscillation frequency and the two outer components to a combination of oscillation and rotational frequencies. However, in the case of gases the central component is always missing, i.e. the oscillation frequencies do not exist alone. Thus the bands are double rather than triple. The duplicity of many of the bands shown above and the possibility that many of the other bands may be unresolved would suggest the possible application of the above theory to liquids.

Of all the bands shown above in Figs. 3 and 4, the 1.38μ band for the methylene halides and for methyl iodide shows the greatest separation. It has been pointed out that this separation is greatest for the iodide. Under the newer quantum theory the rotational frequencies of the gas

molecule occur only in whole multiples, n, of $h/4\pi^2 I$, where h is Planck's constant and I the moment of inertia of the molecule. Thus

$$\nu_r = nh/4\pi^2 I \tag{1}$$

This combination of rotational frequencies with an oscillation frequency gives to the two components of the double band a structure of equally spaced narrow bands, or lines, which under high resolution have been discovered in the cases of some diatomic gases by Imes[9] and others. The separation of these lines is given by ν_r. Now according to Kemble[10] the value of n which gives the line of maximum intensity is given by

$$n_{max} = 2\pi\sqrt{KIT/h} \tag{2}$$

where K is the gas constant and T the absolute temperature. Combination of Eq. (1) and Eq. (2) gives for the maximum frequency in one of these components

$$\nu_{max} = \sqrt{kT/I}/2\pi \tag{3}$$

Since I varies directly with the mass of the molecule, and since I occurs in the denominator of the expression for ν_{max}, we should expect the heavier methylene iodide molecule to have a smaller separation $2\nu_{max}$ between its two components than the bromide or chloride, provided the theory worked out for gases is also applicable for liquids. This, however, is contrary to observation. If the theory does apply to liquids, we have to assume the heavier molecules of methylene iodide to have smaller effective dimensions than the methylene bromide or chloride molecules.

Harmonic relationship with far infra-red bands. An examination of the curves given by Coblentz shows that all the C-H substances have a band at approximately 6.9μ. Out of the large number of characteristic absorption bands this and the one at 3.4μ alone seem to be common to all C-H compounds. This fact has led the writer to conclude that the 6.9μ band is probably a fundamental oscillation band for the carbon-hydrogen linkage. Coblentz has ascribed it and also the 3.4μ band to a CH_2 or a CH_3 group, while Weniger[11] ascribed it to O-H in the case of the numerous alcohols which he investigated.

Possible harmonics in the near infra-red are given in Table III. These values from the third to the seventh check well with the wave-number values for the five bands mentioned above as being characteristic of all the compounds tabulated in Table I.

In computing this table the average values for the wave-numbers of all the substances examined were taken. A progressive variation between

[9] Imes, Astrophs. J. **50**, 1919
[10] Kemble, Phys. Rev. (2), **8**, 1916
[11] Weniger, Phys. Rev., **31**, 1910

the calculated and the observed values is noticed. The second harmonic at 2.3μ shows up in some of Coblentz' curves, much weaker than the first. It lies at one end of the region of the present investigation, and because of the comparatively thick cell used was not clearly defined.

TABLE III

Harmonic	ν(*calc.*)	ν(*obs.*)	λ(*calc.*)	λ(*obs.*)	*Diff.* (*per cent*)
1	290		3.450μ		
2	435		2.300		
3	580	590	1.725	1.696μ	2
4	725	727	1.380	1.375	–
5	870	855	1.150	1.171	−2
6	1015	980	0.975	1.023	−3
7	1160	1105	0.863	0.906	−5

A regular diminution in the intensities would be expected among these bands. In Coblentz' curves the intensities fall off regularly from the fundamental to the first and second harmonics. The present investigation shows a regular diminution with the exception that the fourth and fifth harmonics are of approximately equal intensities, while the seventh is a little stronger than the sixth. The two latter, however, are much weaker than the two former.

In conclusion, the writer wishes to express his thanks to Professor E. P. Lewis, out of whose suggestion this research originated, for his advice throughout the progress of the work. He also wishes to express his appreciation to Professor R. T. Birge for his suggestions concerning the applications of the quantum theory to band spectra.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA,
March 20, 1923.

OBLIQUE SCATTERING OF LIGHT IN GASES AND LIQUIDS

By A. S. Ganesan

Abstract

Oblique scattering of sunlight in gases and liquids.—(1) *Theoretical variation with angle.* The scattered light is assumed to consist of an unpolarized part whose intensity is the same in all directions and a polarized part whose intensity varies as $(1+\cos^2\varphi)$. This leads to simple equations for the ratio of the two components and for the total intensity for various angles, which are found to agree within 5 per cent with the (2) *experimental results for carbon dioxide and for dust-free toluene, benzene and ether.* The observed ratios of the intensity for $\varphi=45°$ to that for $\varphi=90°$, are 1.91, 1.79, 1.71 and 2.12 respectively; the observed ratios of the components for $\varphi=90°$ are .102, .52, .48 and .084 respectively. For *carbon disulphide* the observed ratio is .704.

1. Study of Oblique Scattering in Gases

THE scattering in gases at ordinary pressures is rather feeble, so that unless sufficient precautions are taken, visual determinations of the intensity or of the state of polarization are easily liable to serious errors. To obtain reliable results, two points must be particularly attended to. The incident beam must be very intense and secondly, the back-ground against which the track is viewed must be perfectly black. For this purpose the following arrangements were employed.

Sunlight reflected from a large plate-glass mirror was concentrated by the objective of an astronomical telescope of 18 cm diameter and 200 cm focal length, and then focussed by a second lens of about 20 cm focal length at the centre of the cross tube containing the gas under examination. A very intense illuminating beam was thus secured which enabled the intensity and state of polarization to be quantitatively determined by visual photometry.

To study the scattering at different angles a set of 5 cross tubes were made up of zinc sheet with their arms inclined at angles of 30°, 45°, 60°, 75° and 90° respectively. The ends A, B and C (Fig. 1) were fitted with plane, clear glass windows. At D a glass plate was fixed at 45°, blackened on both sides so that no light was reflected back towards the observer. This end was further wrapped up with dark cloth. An ideal background for these experiments would be Rayleigh's black glass horn, but the arrangement described above was more easily set up and

was found to serve the purpose sufficiently. The cross tubes employed had 8 cm diameter and each arm was of about 20 cm length. They were completely blackened inside and made air tight. To cut off superfluous light, apertures about 3 cm in diameter were placed along the four arms. Two side tubes served to let in and let out the gas. The condensed beam of light was passed along the arm AB and the track was viewed through the observation window C against the background. For quantitative work the observer's eyes must be shielded from all extraneous light. For this purpose the observer locates himself in a canvas cage covered outside by dark cloth, in one of the walls of which is a perforation into which protrudes the observation window C of the cross tube. After remaining some

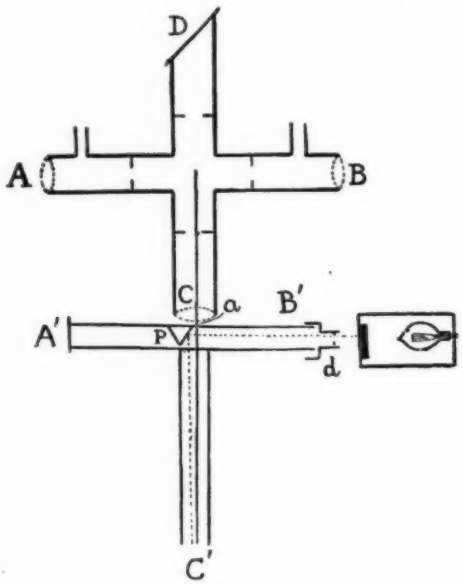

Fig. 1

little time in the cage, even the feeble track of scattering by hydrogen gas is seen as a conspicuous phenomenon. For the purpose of the present study, it was thought sufficient to confine attention to the case of one gas, namely carbon-dioxide, as this shows comparatively intense scattering and exhibits markedly imperfect polarization in the transverse scattering.

The tube was first exhausted and then dust-free carbon-dioxide was passed through it in a continuous stream. The state of the polarization was measured by a double-image prism and nicol. A rectangular aperture punched in a piece of black paper was placed in front of the observation window and the double-image prism adjusted to give two images of this aperture illuminated by the scattered light and polarized respectively

in vertical and horizontal planes. The two positions of the nicol placed behind the prism were found for which the two images were of equal brightness. If 2θ be the angle between these two positions of the nicol, the ratio of the intensities of the two components is given by $\tan^2\theta$.

The intensity of the scattered light in different directions was measured by comparing the track with a standard source of light. The light from a 50 c.p. Osram lamp filtered through blue glasses of sufficient thickness to secure a color-match with the blue of molecular scattering, was passed through an adjustable aperture (an iris diaphram of an ordinary camera was found very suitable) on to the face of the photometric wedge which consisted of a strip of white filter-paper held at an angle. Fig. 1 shows the arrangement.

$A'B'C'$ is a hollow wooden T piece of about 5 cm square cross-section, the two arms being each 30 cm long. At B' is fixed the adjustable diaphram. The photometric wedge P is fixed at the centre of the cross arm adjacent to the small aperture a which is placed against the face C of the cross tube through which the track is viewed. The T piece is completely blackened inside. By adjusting the diaphram the two spots (the aperture illuminated by the track, and the white patch illuminated by the blue light from the lamp) are made of equal brightness.

TABLE I

Polarization of light scattered by carbon dioxide

Ratio of components			Ratio of components		
ϕ	Obs.	Calc.	ϕ	Obs.	Calc.
30°	75.9 %	77.6%	105°	17.3%	16.2%
45°	55.6	55.1	120°	32.5	32.6
60°	30.0	32.6	135°	52.6	55.1
75°	16.0	16.2	150°	79.4	77.6
90°	10.18				

TABLE II

Intensity of light scattered by carbon dioxide

ϕ	Observed	Calculated
90°	1	
60°	1.34	1.38
45°	1.91	1.98

The calculated values given in the above two tables are obtained as explained in section 3 of this paper.

2. STUDY OF OBLIQUE SCATTERING IN LIQUIDS

The study of scattering in liquids is made in the same manner as in the case of gases. Here the track being more intense the experimental diffi-

culties are less. The liquids are contained in large glass bulbs. They are made dustfree by repeated slow distillations in vacuo using the form of apparatus devised by W. H. Martin.[1] The bulb is completely blackened except for three windows for the ingress and egress of light and for making the observations. Sunlight reflected from a mirror is focussed by means of a short-focus lens at the centre of the bulb. A rectangular aperture is placed in front of the bulb, and as before the polarization is measured by means of the double image prism and nicol. The bulb is placed at the center of a graduated circle while the combination of the double image prism and nicol moves along the graduations, thus enabling measurements to be taken at various angles.

To measure the intensity, two beams of light reflected by two similar mirrors and focussed by two lenses of the same focal length are made to cross at the centre of the bulb one above the other. They are viewed in a direction perpendicular to one of the tracks. In the path of the two beams apertures are placed and by adjusting them the two tracks are made equal. The intensities are inversely proportional to the areas of the apertures. By altering the angle between the two crossing beams the intensity can be measured in different directions. Care is taken to reflect the sunlight from the mirrors at nearly the same angles. In the case of benzene which was contained in a cylindrical bottle, the intensities of the crossed beams were directly compared by means of a rotating sector photometer which yielded very satisfactory results.

The following tables give the results obtained with carbon disulphide, toluene, benzene and ether, all Merck's extra pure quality and made absolutely dust free.

TABLE III

Observed and calculated ratios of two polarized components for light scattered by various liquids in various directions, in percent.

ϕ	Carbon disulphide		Toluene		Benzene		Ether	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
40°			81.7	80.2	82.2	78.5	63.7	62.2
50°	84	82.6	73.4	71.9	75.8	69.5	47.2	46.3
60°	79.2	77.8	63.7	64.1	61.5	61.0	32.3	31.3
70°	75.6	73.9	56.4	57.8	56.8	54.1	19.6	19.2
80°	73.0	71.3	53.2	53.6	50.1	49.6	11.6	11.2
90°	70.4		52.2		48.0		8.44	
100°	70.9	71.3	52.4	53.6	48.7	49.6	10.3	11.2
110°	73.0	73.9	55.2	57.8	54.4	54.1	18.6	19.2
120°	76.6	77.8	61.5	64.1	60.2	61.0	30.7	31.3
130°	81.1	82.6	69.9	71.9	68.4	69.5	50.9	46.3

[1] Martin, Journal of Physical Chemistry, 1919

TABLE IV

Intensity of light scattered by various liquids in different directions

ϕ	Toluene		Benzene		Ether	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
90	1		1		1	
60	1.377	1.246	1.321	1.257	1.423	1.399
45	1.788	1.636	1.708	1.663	2.120	2.011
30	2.557	2.471	2.626	2.527	3.312	3.267

In the case of benzene the observed values with the rotating sector photometer were 1.200, 1.612 and 2.472 respectively in the three directions. The calculated values in the above tables are obtained after the manner explained in the following section.

3. Theory of Oblique Scattering in Fluids

The imperfect polarisation of the transversely scattered light by gases has been explained by Lord Rayleigh, Born and others as due to molecular anisotropy. A complete mathematical theory has been developed by Ramanathan[2] which includes the case of both gases and liquids on the assumption that the *orientation* of the molecules is at random. For our present purpose, the matter may be dealt with on a purely geometrical basis, and a simple formula may be obtained in the following way. When the incident light is unpolarised we may consider the scattered light as consisting of two parts, one consisting of polarised light whose intensity varies according to the law $(1+\cos^2\phi)$, and a second part consisting of unpolarised light whose intensity is the same whatever be the direction in which the light is viewed. Resolving the vibrations corresponding to these in perpendicular directions and denoting the intensities corresponding to the unpolarised and polarised parts by A and B respectively, we have in the transverse direction the ratio between the weak and strong components given by

$$r=A/(A+B).$$

In any other direction ϕ this ratio is given by

$$r_\phi=(A+B\cos^2\phi)/(A+B)=r\sin^2\phi+\cos^2\phi \qquad (1)$$

The values given in Tables I and III are obtained with this formula.

As regards the intensity, that of the polarised part is given by $B(1+\cos^2\phi)$ and adding to this the intensity due to the unpolarised light which is $2A$, (since both the horizontal and vertical components are to be

[2] Ramanathan, Proc. Indian Assoc. Cult. Sci., **8**, I, pp. 1-24

taken), we have the ratio of the intensity in a direction ϕ to the intensity in the transverse direction given by

$$\frac{2A+B(1+\cos^2\phi)}{2A+B}=1+\frac{1-r}{1+r}\cos^2\phi.$$

A correction is to be applied to this for the thickness of the layer of the fluid contributing to the luminosity. In a direction ϕ the ratio of this thickness to the thickness in the normal direction is cosec ϕ so that finally we have

$$I_\phi=\left[1+\frac{1-r}{1-r}\cos^2\phi\right]\operatorname{cosec}\phi. \qquad (2)$$

The calculated results in Tables III and IV are obtained with this formula. It will be seen that the agreement is generally satisfactory.

In conclusion I have to thank Prof. Raman for the great interest he took during the course of the experiments and for his valuable suggestions.

210, Bowbazaar Street,
Calcutta, India,
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EFFECT OF A RETARDING PLATE ON WHITE LIGHT INTERFEROMETER FRINGES

By Nihal Karan Sethi

Abstract

White-light fringes given by the Michelson's interferometer are usually but few in number, and are seen as straight bands. But the mere introduction of a thick glass plate with plane-parallel sides in the path of one of the interfering beams is shown to bring into view literally hundreds of them in the form of circular rings. Any attempt at partially monochromatizing the light diminishes their number. This increase in number is due to the different parts of the spectrum producing interference in different places, as is demonstrated by spectroscopic examination of the rings. The corresponding formulas are quantitatively verified by using them to determine the dispersion of the glass plate employed. Two other examples of this peculiar dispersion of white-light fringes are quoted and it is pointed out that the increase in the number of white-light fringes observed by Wood on introducing sodium vapor into the interferometer path also involves the same process and is not due to achromatization as suggested by him.

Sensitiveness of the eye to color contrast.—These fringes are seen merely by color-contrast. The color has been calculated and is shown to be poorer than even the first order white of Newton's scale and yet the eye is able to distinguish them quite clearly.

IT IS well-known that when Michelson's interferometer is so adjusted that the path-difference between the two beams is zero and white light is used, only a few fringes showing vivid colors as in Newton's rings may be observed, beyond which on either side, the field shows merely uniform illumination; also when a *thin* plate of some transparent substance is introduced into one of the paths, this system of fringes appears to shift as a whole without any change in their number or appearance except that the central fringe is shifted to a slightly greater extent and is no longer strictly achromatic. The same is also true of the white-light fringes formed in any other way, e.g. by means of a bi-prism or a Lloyds' single mirror. It is proposed in this paper to describe and explain certain remarkable effects to which, so far as the writer is aware, attention has not previously been drawn and which are noticed with the Michelson's interferometer when white light is used and a *thick* retarding plate of glass with plane-parallel sides is introduced in the path of one of the interfering beams.

The effects referred to are most conveniently observed by adjusting the interferometer mirrors to give circular fringes with monochromatic light

and viewing them through a telescope. The monochromatic light-source is then removed and white light substituted for it. The thick, retarding plate is now introduced and the movable mirror adjusted till the retardation due to the glass plate is compensated by an increase of the air-path of the other beam. On continuing to move the mirror slowly in the same direction, faintly colored rings make their appearance in the telescope and an astonishingly large number of them, literally hundreds, can be seen before the mirror has advanced too far and the whole field is once more uniformly illuminated. The actual number of the rings that can be observed depends on the thickness of the retarding plate used. A crown-glass plate 1 mm thick gives about 100 rings, while one about 15 mm thick gives over a thousand. Much greater thicknesses have not been tried, but it appears probable that it would not be difficult to observe three or even four thousand of these rings. It is not necessary for this experiment to have any extra plane-parallel glass plate; for we can manipulate the interferometer plates themselves so as to permit of our introducing more glass in one path than in the other. If we require only small thicknesses, we may merely rotate the compensating plate through a suitable angle. This will make the rings rather elliptical but there is no harm in it. If we want larger thicknesses, we may remove the compensating plate altogether so that one beam travels through the half-silvered plate thrice and the other only one. Or we may merely reverse the half-silvered plate so that its unsilvered side faces the compensating plate, the excess of glass in one path over the other being in this case four times the effective thickness of either of the plates.

The white-light fringes obtained in this manner show a number of remarkable features: (1) Their angular diameters are quite small, so that we have a large number of complete rings simultaneously in the field of view. Such a thing is not possible with the white light fringes obtained in the usual manner.

(2) Their diameters decrease with the motion of the interferometer mirror much more rapidly than when monochromatic light is employed.

(3) The visibility of the rings measured in terms of the difference in total intensity of illumination in the maxima and minima appears to be very poor. There are no rings which can be described as black or even as tolerably dark.

(4) The colors of the maxima change continuously with the motion of the interferometer mirror, passing gradually from red to orange, yellow, green, blue and then violet. The minima have colors more or less complementary to those of the neighboring maxima.

(5) On attempting to partially monochromatise the white light used in the experiment by passing it through colored screens, the total number of the visible rings is actually *diminished*. Highly non-homogeneous white light seems to be better for this curious experiment in interference than even the almost completely monochromatic light of the sodium flame, for with this latter, one cannot observe more than a thousand rings continuously without passing through regions where the fringes disappear on account of overlapping. There is, however, one advantage of the use of these colored screens; the fringes appear to gain considerably in contrast in those regions where the maxima had the same color as the screen, although they disappear altogether in other places. Consequently with differently colored screens they are seen in different parts of the field.

Perhaps the simplest method of explaining these effects is to regard a pulse of white light as made up of a large number of differently colored simple groups each of which is associated with certain trains of waves of mean wave-length λ. It is well-known that through air these groups travel with nearly the same velocity as the individual waves of which they are formed, but in a dispersive medium like glass, they travel more slowly with a velocity

$$U = V - \lambda dV/d\lambda \qquad (1)$$

where V is the velocity in the same medium of waves of wave-length λ, and that the central band in the fringes formed by one of these groups will not appear when the path-difference for the waves is zero, but only when the *groups* traveling along the two interferometer paths arrive simultaneously in the eye, i.e. when the retardation suffered by the group on account of its passage through the glass plate is exactly compensated by an alteration of the air-path. This condition gives

$$2t/V_0 = 2D/U - 2D/V_0 \qquad (2)$$

where V_0 is the velocity of the group in air, D is the thickness of the glass plate and t is the distance through which the interferometer mirror is shifted from the usual position in which it gives an achromatic fringe with white light.

From this it is evident that unless D is very small the value of t should differ considerably for groups belonging to the different parts of the spectrum, so that even when the interferometer mirror is moved through a considerable distance within a certain range, the region of maximum visibility for the fringes formed by some one part of the spectrum always remains in the field of view. In the arrangement with the half-silvered plate reversed as described above, this range is well over 0.3 mm and thus we are able to see over 1000 fringes showing the succession of colors mentioned above.

On reduction Eq. (2) becomes

$$t-(\mu-1-\lambda\, d\mu/d\lambda)\, D=0 \qquad (3)$$

where μ is the refractive index of the glass plate.[1] The order of interference n is then given by

$$n=\frac{2t-2(\mu-1)D}{\lambda}=2D\,\frac{d\mu}{d\lambda}.$$

In the case of a glass plate 1.7 cm thick, this makes n of the order of 1700 for the middle of the spectrum, and it is this interference of a high order which explains the small diameter of the rings observed in this experiment.

In order quantitatively to verify relation (2) or (3) or its equivalent

$$t-(A-1+3B/\lambda^2)\, D=0$$

or

$$t_2-t_1=3BD(1/\lambda_2^2-1/\lambda_1^2) \qquad (4)$$

obtained by putting

$$\mu=A+B/\lambda^2,$$

the fringes were focussed by means of a lens on the slit of a wave-length spectrometer. The spectrum showed a system of rings in some one part surrounded on either side by narrow arcs which soon became too fine to be observed. When the slit was not fine, only about a dozen rings or parts of rings could be seen on an otherwise continuous spectrum. The exact shape of these rings obviously depends on the dispersion of the spectroscope and the focal length of the lens used for focussing the fringes on the slit, but they generally appear more or less elliptical. By altering the position of the interferometer mirror, the center of these rings changes its position continuously from one end of the spectrum to the other. The formation of the closed curves in one part of the spectrum showed that condition (2) was satisfied in this region. By noting on the spectrometer drum the wave-length reading of the center of the rings, and the corresponding position of the interferometer mirror, we can get all the data necessary for finding from relation (4) the value of B for the glass plate used. The following table shows the value obtained by this

TABLE I

Position of mirror	Wave-length at the center of the rings	B (Calc.)	B from Hilger's data
1.18893 cm	$4.555\,(10)^{-5}$cm		
1.19054	4.678	$4.59\ (10)^{-11}$	
1.19446	5.060	4.16	
1.19839	5.560	4.15	
1.20074	5.960	3.97	
1.20272	6.392	3.79	
	mean:	$4.132\,(10)^{-11}$	$4.156\,(10)^{-11}$

[1] See Lord Rayleigh, Phil. Mag. Sept. 1904 and Scientific Papers Vol. V.

method and that given by Hilger's data in the case of a Lummer-Gehrcke plate 4.716 mm thick placed normally as in the usual method. Considering the necessarily rough setting for the center of the rings, the agreement is fairly good.

It is a noteworthy fact that although these fringes are so easily and clearly visible to the eye, they cannot be so easily photographed. At least the writer has not yet succeeded in getting any trace on the photographic plates. This may be due to the fact that in this case, the whole of the spectrum except a very narrow region for which condition (2) is satisfied, produces uniform illumination all over the field and the change in total intensity between the maxima and minima is very small. The eye is able to see them on account of its wonderful power of detecting small changes in color specially when suitably presented.

It may be interesting in this connection to actually calculate the color-contrast of the maxima and minima by determining in each case the relative intensities of the three primary color-sensations according to the method used by Rayleigh for the colors of thin plates.[2]

The result in the case of a plate 1.7 cm thick showing over 1000 fringes is shown below. The region of maximum visibility is at 5500 A. The components of full white and of the first order white on Newton's scale are also given for comparison.

TABLE II

	Red	*Green*	*Violet*
Maxima	4.02	6.72	6.46
Minima	3.95	6.41	6.46
First order white	3.97	6.86	6.46
Full white	3.97	6.52	6.46

It is not convenient to express this result on Maxwell's color triangle, for the points representing these colors are too close together. But it is evident that the colors are poorer than even the first order white which is according to Lord Rayleigh "somewhat greenish, but the deviation from full white is very small and is not usually recognized."[2] But in the present case, by the mere fact of two such colors being placed side by side, one slightly greenish and the other slightly pinkish, the eye is able to appreciate them quite easily.

In his paper on the achromatization of approximately monochromatic interference fringes by a highly dispersive medium, R. W. Wood[3] has described an experiment in which sodium vapor was introduced into one of the interferometer paths. It was found that the number of the white-

[2] Rayleigh, Edin. Trans. **33**, 1886 and Scientific Papers, Vol. II, p. 498

[3] R. W. Wood, Phil. Mag. Sept. 1904 and Physical Optics, Second Ed. p. 141

light fringes had considerably increased and they had moreover broken up into several groups. This latter effect was explained by him as being due to anomalous dispersion of the vapor, but the increase in the number of fringes does not appear to have been fully explained. The similarity between his experiment and the one described in this paper is obvious and the increase in the number of the fringes must be due as here, to the formation of the fringes by the different parts of the spectrum in different places. The process involved can in no sense be called achromatization, which if perfect, should give the maxima due to all the parts of the spectrum exactly superposed so as to produce black and white fringes of perfect visibility. Even if it is imperfect, this condition should be satisfied for a major portion of the spectrum at least in some part of the field. In fact the process is just the reverse of achromatization and may be described more appropriately as the dispersion of the achromatic band. The same process is involved in the increase in the number of white-light fringes produced by a Lloyd's mirror when a thick glass plate is introduced into one path and an equal thickness of a mixture of carbon disulphide and benzene of nearly the same refractive index into the other.[4] Yet another example is the case of white-light fringes produced by a wedge-shaped plate and observed through a prism. The late Lord Rayleigh[5] had definitely shown that no achromatic system of fringes is possible in this case and in his opinion the succession of colors and the number of perceptible fringes cannot be altered by the prism unless the surfaces forming the plate were slightly curved. The present writer[4] has, however, shown both theoretically and experimentally that while achromatization is not possible, the dispersion of the white-light fringes can be brought about exactly as in the case discussed in this paper, and even with a wedge-shaped plate we can have a very large number of visible fringes formed between thick interferometer plates.

The writer is greatly indebted to Prof. C. V. Raman for his interest in the work.

THE PHYSICAL LABORATORY,
BENARES HINDU UNIVERSITY,
May 2, 1923.

[4] Sethi, Proc. Indian Assn. Cult. Sci. **7**, 37, 1921
[5] Rayleigh, Phil. Mag. **28**, 1889 and Scientific Papers III, p. 313

SCATTERING OF PARTICLES BY AN EINSTEIN CENTER

By W. S. Kimball

Abstract

Relativity theory of the scattering of atomic rays by a nucleus.—The Coulomb inverse square law of force is replaced by Einstein's law corresponding to a fixed point center, and the Schwartzschild solution of the field equations of gravitation is used, taking the constant of integration which measures the strength of the center as purely electrical in nature and equal to NeE/c^2M instead of $\gamma m/c^2$, the Einstein center being thus used to account for Coulomb's law instead of Newton's law as in the relativity theory of gravitation. No attempt is made to combine gravitational and electrical terms in the potentials such as developed by Jeffery and Nordstrom. The resulting formula agrees with Rutherford's except that there are added to the factor $\cot^2\phi/2$, ϕ being the angle of deflection, terms in V^2, V^4, etc. where V is the velocity of the ray divided by that of light. The result is that the scattering is no longer accurately proportional to $1/V^4$ nor to $\cot^2\phi/2$. However for values of V to 1/15 or 2×10^9 cm/sec., the departures are less than one per cent, that is less than the probable error of the experimental results; but an accuracy of 1/1000 would decide between the two theories.

THE object of this paper is to consider the scattering of a stream of particles when the inverse square law of force is replaced by Einstein's law corresponding to a fixed point center. Rutherford[1] and Darwin[2] have developed formulas based upon the inverse square law which account for the scattering of α-particles and hydrogen atoms to a high degree of accuracy. Professor Lunn suggested that a comparison be made with the results due to an Einstein point center, Coulomb's law for the forces within the atom being replaced as Newton's law is in the gravitation theory, by a non euclidian space-time symmetrical about the center. Formulas are developed herein which admit of a comparison of the scattering of α-particles required by the inverse square law with the scattering when this law is replaced by Einstein's law. The results show that so far as α-particles are concerned, the theoretical difference in scattering in the two cases is too minute to be detected by the available experimental data.

The properties of the space-time about a point center are determined by Schwartzschild's form

$$ds^2=dt^2(1-2l/r)-dr^2/(1-2l/r)-r^2d\theta^2-r^2\sin^2\theta d\phi^2.$$

[1] Rutherford, Phil. Mag. **21**, 670, (1911)
[2] Darwin, Phil. Mag. **27**, 499, (1914)

Here l is the constant of integration which measures the strength of center. It is of dimensions of length and in the gravitation theory $l=\gamma m/c^2$, where γ is the gravitation constant, m, the mass of the center and c, the velocity of light. In this paper l is assumed to be purely electrical in nature, no attempt being made to combine gravitational and electrical terms in the potentials such as developed by Jeffery[3] and Nordstrom.[4] The above value of l in the gravitation theory for an uncharged center gives an orbit which is a close approximation to that due to Newton's law: $f=\gamma mM/r^2$. The corresponding substitute for Coulomb's law with dielectric constant unity, replaces $\gamma mM/r^2$ by NeE/r^2, and hence makes $l=NeE/c^2M$. This value of l gives rise to an orbit which approximates that due to Coulomb's law, just as the above choice of l in the gravitation theory gives an approximation to Newton's planetary orbits. It is the value of l so determined that is used here.

The study of paths due to an attracting force is made in parallel with the study of paths due to a repelling force, though we shall limit ourselves in regard to the former, to the cases where the orbits extend to infinity. Forsyth[5] has shown that in the case of an attracting center, the equations of the path may be expressed in elliptic functions, and Morton[6] has given a classification of these orbits. From a mathematical point of view the present paper is a study of the relations between d, the perpendicular from center of force to asymptote, and ϕ, the angle of deflection of the moving particle.

The differential equations of motion of a free particle under the relativity theory are those of geodesics for the 4-space under consideration. The equation for the repelling center is obviously obtained by changing the sign of the constant of the center, wherever this l appears in the equations of motion due to an attracting center. This latter is well known and need not be derived here.

1. Case I. *Repelling center*

$$\frac{du}{d\theta}=\sqrt{-2lu^3-u^2-\frac{2lu}{h^2}+\frac{V^2}{h^2}}. \tag{1}$$

Case II. *Attracting center*

$$\frac{du}{d\theta}=\sqrt{2lu^3-u^2+\frac{2lu}{h^2}+\frac{V^2}{h^2}}. \tag{2}$$

[3] Jeffery, Proc. Roy. Soc. London **99**, 123 (1921)
[4] Nordstrom, Proc. Ac. Amsterdam **20**, 1236 (1918)
[5] Forsyth, Proc. Roy. Soc. **97**, 145 (1920)
[6] Morton, Phil. Mag. **42**, 511 (Oct. 1921)

where $u=1/r$, and θ is the polar angle, and h is the constant of areas, and V is the initial velocity of the particle; at infinity. V^2 is determined by a constant of integration and is positive and hence V is real for all orbits considered in this paper, that is orbits extending to infinity. This includes all possible orbits for Case I.

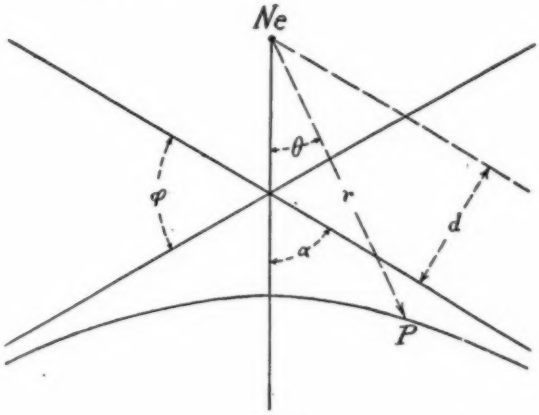

Fig. 1

2. If the cubics of the right hand members of (1) and (2) are set equal to zero, the three roots will correspond to apsidal distances in the orbits. Since the equations thus obtained are identical for (1) and (2) except for the sign of the odd powers of the variable, the roots of the two equations will be equal except for sign. Let them be: for Eq. (1), a_1, $-a_2$, $-a_3$; and for Eq. (2) $-a_1, a_2, a_3$; where $a_3>a_2>a_1>0$. Then a_1 is the reciprocal of the only apsidal distance for Case I, and a_2 is the reciprocal of the only apsidal distance for Case II. If these equations are solved for h^2 in terms of the roots, we obtain

$$\text{for Case I} \quad h^2=\frac{V^2-2la_1}{a_1^2(1+2la_1)}; \tag{3}$$

$$\text{for Case II} \quad h^2=\frac{V^2+2la_2}{a_2^2(1-2la_2)}. \tag{4}$$

3. The distance of nearest approach of two repelling particles moving on a fixed line towards each other comes from Eq. (3) with the special condition that $h=0$:

$$b=1/a_1=2l/V^2=2NeE/c^2MV^2 \tag{5}$$

This constant is of the same form as the corresponding constant for inverse square orbits.

4. A study of Eq. (2) will show that real "hyperbolic" orbits are only possible for Case II when all three roots are real. If $u+a_1$ is factored out

of the right hand member of (2) by long division, the discriminant of the resulting quadratic,

$$u^2+u(1/2l+a_1)+1/h^2+a_1(1/2l+a_1)=0$$

determines the reality of the other two roots, a_2, and a_3. The vanishing of the discriminant of this equation thus determines a limiting value of h^2. The root a_1 may be eliminated from the expression of h^2 so determined by using the relations between the roots given by the theory of cubic equations with two equal roots. Thus

$$h_0^2=\frac{32l^2}{1-18V^2-27V^4+(1+9V^2)^{\frac{1}{2}}\,(1+V^2)^{\frac{1}{2}}} \tag{6}$$

This is the smallest possible constant of areas that a "hyperbolic" orbit due to an attracting point center can have for a given V and l.

5. The integral equations of the path are expressible by elliptic functions:

$$\text{(I)}\quad sn\tfrac{1}{2}\theta\cdot\sqrt{2l(a_1+a_3)}=\sqrt{(a_1-u)/(a_1+a_2)};\ k^2=\frac{a_1+a_2}{a_1+a_3};\ h>h_0 \tag{7}$$

$$\text{(II)}\quad sn\tfrac{1}{2}\theta\cdot\sqrt{2l(a_1+a_3)}=\sqrt{\frac{(a_2-u)\ (a_1+a_3)}{(a_3-u)\ (a_1+a_2)}};\ k^2=\frac{a_1+a_2}{a_1+a_3};\ h>h_0 \tag{8}$$

$$\text{or (I)}\quad cn\theta\cdot\sqrt{2H}=\frac{(H-a_1+u)}{(H+a_1-u)};\ H^2=a_1/l+3a_1^2+1/h^2;\quad h>0;\quad k^2=(2H+\tfrac{1}{2}l+3a_1)/4H. \tag{9}$$

$$\text{(I)}\quad p(\theta)=\frac{\frac{1}{2}l(3a_1^2+a_1/l+1/h^2)}{a_1-u}-(\tfrac{1}{2}la_1+\tfrac{1}{12})=\frac{(e_3-e_1)\ (e_2-e_1)}{-(e_1+1/12+\frac{1}{2}lu)}+e_1;$$
$$g_2=1/12-l^2/h^2;\ g_3=1/216-l^2/4h^2(\tfrac{1}{3}+V^2). \tag{10}$$

$$\text{(II)}\quad p(\theta)=\frac{\frac{1}{2}l(3a_2^2-a_2/l+1/h^2)}{u-a_2}+\tfrac{1}{2}la_2-\tfrac{1}{12}=\frac{(e_3-e_2)\ (e_2-e_1)}{e_2+1/12-\frac{1}{2}lu}+e_2;$$
$$g_2=1/12-l^2/h^2;\ g_3=1/216-l^2/4h^2(1/3+V^2). \tag{11}$$

The verification of these equations of the path is made by solving for u in each case and substituting this value of u in Eq. (1) or (2), and using the indicated value of the parameters k^2, g_2, or g_3. For Jacobi's elliptic functions, the substitution by means of (7), (8) or (9) gives the Jacobi canonical form of the elliptic integral. For Weierstrass's elliptic functions, the substitution by means of (10) or (11), transforms (1) or (2) to the Weierstrass canonical form.

6. The orbit due to an attracting center can be derived from an orbit due to a repelling center, and vice versa, in a way similar to that which obtains in the classical theory with the inverse square law of force, by changing the sign of $u=1/r$ and adding half a period (K or ω_3) to the argument of the elliptic function.

Eq. (7) may be written:

$$snA=\sqrt{(a_1-u)/(a_1+a_2)}$$

where A stands for argument. It is well known that $sn(A+K)=cnA/dnA$. From (7) $cn^2A=1-(a_1-u)/(a_1+a_2)=(a_2+u)/(a_1+a_2)$; and $dn^2A=1-(a_1+a_2)(a_1-u)/(a_1+a_3)(a_1+a_2)=(a_3+u)/(a_1+a_3)$. Therefore $sn(A+K)=\sqrt{(a_2+u)(a_1+a_3)/(a_3+u)(a_1+a_2)}$, which is a way of writing (8) provided the sign of u in (8) is changed. Similarly the half period formula applied to (8) reduces it to (7) except for the sign of u.

In the Weierstrass notation the half period formula is

$$p(\theta+\omega_3)=\frac{(e_3-e_2)\ (e_3-e_1)}{p(\theta)-e_3}+e_3.$$

If $p(\theta)$ appearing in it is replaced by (10), this formula reduces to

$$p(\theta+\omega_3)=\frac{(e_3-e_2)\ (e_2-e_1)}{e_2+1/12+\frac{1}{2}lu}+e_2.$$

The right hand member of this equation is the right hand member of (11) except for the sign of u. Similarly (11) substituted in the half period formula gives (10), except for the sign of u.

7. If $u=0$ the orbit extends to infinity and θ approaches a limiting value or asymptotic angle α. Hence

$$\text{(I)}\quad sn\tfrac{1}{2}\alpha\sqrt{2l(a_1+a_3)}=\sqrt{a_1/(a_1+a_2)};\ \text{or}\ cn(\alpha\sqrt{2lH})=(H-a_1)/(H+a_1) \tag{12}$$

$$p(\alpha)=la_1+5/12+l/2h^2a_1$$

$$\text{(II)}\quad sn\tfrac{1}{2}\alpha\sqrt{2l(a_1+a_3)}=a_2(a_1+a_3)/a_3(a_1+a_2) \tag{13}$$

$$p(\alpha)=5/12-la_2-l/2h^2a_2.$$

Note that in Case I $p(\alpha)$ is always greater than 5/12 since ', h^2, and a_1 are all greater than zero; and that for a similar reason $p(\alpha)$ is always less than 5/12 in Case II. It will presently appear that if $p(\alpha)=5/12$ for the g_2 and g_3 in question, $\alpha=\frac{1}{2}\pi$.

8. Limiting cases of $p(\alpha)$ occur when $g_2^3=27g_3^2$; the discriminant of the cubic in Weierstrass' differential form is zero, and two roots are equal. Two cases arise:

(a) $e_1=e_2<0$, $p(\alpha)$ degenerates to a circular function with real period only. $(e_3=1/6;\ e_1=e_2=-1/12;\ h^2=\infty)$. $d\alpha=ds/\sqrt{4(s-e_2)^2(s-e_3)}$ when integrated by elementary methods gives: $s=e_3+(e_3-e_2)\cot^2\alpha\sqrt{(e_3-e_2)}$; or introducing the above values of the roots

$$s=p(\alpha)=\frac{5}{12}+\frac{\cos\alpha}{2(1-\cos\alpha)}. \tag{14}$$

(b) $e_3=e_2>0$, $p(\alpha)$ degenerates to a hyperbolic function with imaginary period only. $d\alpha=ds/\sqrt{4(s-e_2)^2(s-e_1)}$, when integrated by elementary methods gives

$$s=p(\alpha)=e_2+(e_2-e_1)\ \mathrm{csch}^2\alpha\sqrt{(e_2-e_1)}. \tag{15}$$

9. The range of d, the perpendicular distance from center of force to asymptote and α, the asymptotic angle.

(a) $h=\infty$. This is the limiting case of §8 (a). Since $h=Vd$ and $V>0$, d must be infinite. In this case $e_1=e_2=-1/12$ and $a_1=a_2=0$, as may be shown from the relations between the roots in question. It follows that the orbit is at all times at infinite distance from the center of force. It also appears from (12) and (13) that $p(\alpha)=5/12$ in both Case I and Case II. And from (14), the asymptotic angle α is equal to $\pi/2$, and both orbits are thus rectilinear and at infinite distance from the center of force.

(b) $h=h_0$. This is the limiting case of §8 (b), where $e_2=e_3$, and $d=d_0$. The situation is quite different for Case I and for Case II. For the latter, (13) shows, since $a_2=a_3$, that both modular angle and amplitude of Jacobi's elliptic functions are $\pi/2$. Therefore $\alpha=\infty$.

For Case I, $h=h_0$ has no significance. Formulas (12) hold equally for this orbit whether $h>h_0$ or $h<h_0$, except that for $h<h_0$ the second form of the equation in Jacobi functions must be used since a_2 and a_3 are then conjugate imaginaries that become infinite in the limiting case when $h=0$ and $a_1=V^2/2l$. In this case, by Eq. (12), $p(\alpha)=\infty$, and hence $\alpha=0$. Thus:

Case I. Range of d is from 0 to ∞, with corresponding range of α from 0 to $\pi/2$.

Case II. Range of d is from ∞ to d_0, with corresponding range of α from $\pi/2$ to ∞.

10. To study scattering formulas, we require the relation that exists between d, the perpendicular distance from the center of force to the asymptote, and α, the asymptotic angle. The method of getting this is to eliminate the roots between (3) and (12) for Case I or between (4) and (13) for Case II. It was found to be impossible to carry out this elimination using Jacobi elliptic functions, so the Weierstrass functions are used, the result being an expression for h or d in terms of $p(\alpha)$. If $p(\alpha)$ is expanded and account taken of (14), it is possible by a rather lengthy mathematical development to express h or d as a power series in powers of V^2 with coefficients that are trigonometric functions of α the asymptotic angle, except for very small terms. Thus:

$$d^2=\tfrac{1}{4}b^2[\tan^2\alpha+V^2\left\{\frac{2(1-\cos\alpha)^2(2+\cos\alpha)}{\cos^2\alpha\,(1+\cos\alpha)}+\frac{4(1-\cos\alpha)S}{\cos\alpha(1+\cos\alpha)}\right\}+V^4\{....\}+... \tag{16}$$

where $S=\alpha^2/20+\alpha^4/12\cdot 28+\frac{1}{4}V^2\alpha^4/28+\alpha^6/5^2\cdot 3^2\cdot 2^5-\ \ldots\ .$

Expression of d^2 is shown to be convergent for values of $\alpha<\pi/2$ by comparison of values given by it with values of d^2 given by the first obtained expression for d^2 in terms of $p(\alpha)$, whose expansion is known to be convergent. Since the velocity of light is taken as unity, V^2 will have for the highest speed α-particles a value in the neighborhood of 1/225, so that (16) will in general converge very rapidly. For $\alpha=(2n+1)\pi$ this formula will diverge, so it is not useful for Case II where the range of α is from $\pi/2$ to ∞.

11. The scattering formula derived by Rutherford and extended by Darwin is based upon probability considerations:

$$q=\pi d^2nt, \tag{17}$$

where q = probability that particle will pass within distance d of center of an atom; n = number of atoms per cc of metal foil; t = thickness of the foil. Attention is restricted to simple as distinct from compound scattering, i.e., to the case where the foil whose atoms cause the scattering of α-particles is so thin that secondary collisions after the first encounter are so few in number as to be negligible. Rutherford's formula comes direct from (17) by replacing d, the perpendicular from center of force to the asymptote by its value in terms of the angle of deflection calculated from the inverse square law, or true hyperbolic orbit:

$$d=\tfrac{1}{4}b\tan\alpha=\tfrac{1}{2}b\cot\tfrac{1}{2}\phi, \tag{18}$$

where b = distance of nearest approach of particle to nucleus when approaching directly on a line; ϕ = angle of deflection, $\frac{1}{2}\phi=\frac{1}{2}\pi-\alpha$.

Note that the formulas (16) and (18) for d^2, given by the relativity theory and the classical theory are the same to first approximation, the zero power term in the expansion (16) being identical with (18).

From (17) and (18) the scattering, or fraction of the beam of particles deflected between angles ϕ_1 and ϕ_2 is

$$\rho=\tfrac{1}{2}\pi ntb^2(\cot^2\tfrac{1}{2}\phi_1-\cot^2\tfrac{1}{2}\phi_2), \tag{19}$$

where $b=2NeE/MV^2$, from energy equation. Thus the scattering due to inverse square forces is seen to be proportional to:

(1) number of atoms per cc in the substance of the foil;
(2) thickness of the foil;
(3) the square of the nuclear charge;
(4) the reciprocal of the 4th power of the velocity;
(5) the square of the cotangent of the half angle of deflection.

12. It is obvious that (17) holds just as it stands for a relativity law of force as well as an inverse square law, since it arises out of a situation beyond the scope of atomic forces, d being the perpendicular to the

asymptote. To get the relativity scattering formula, d is accordingly eliminated between (17) and (16) instead of between (17) and (18), (since $\alpha=\frac{1}{2}\pi-\frac{1}{2}\phi$).

$$\rho=\tfrac{1}{4}\pi ntb^2[(\cot^2\tfrac{1}{2}\phi_1-\cot^2\tfrac{1}{2}\phi_2)+V^2\Big\{\frac{2(1-\sin\frac{1}{2}\phi_1)^2(2+\sin\frac{1}{2}\phi_1)}{\sin^2\frac{1}{2}\phi_1(1+\sin\frac{1}{2}\phi_1)}+ \tag{20}$$

$$\frac{4(1-\sin\tfrac{1}{2}\phi_1)S_1}{\sin\frac{1}{2}\phi_1(1+\sin\frac{1}{2}\phi_1)}-\frac{2(1-\sin\frac{1}{2}\phi_2)^2(2+\sin\frac{1}{2}\phi_2)}{\sin^2\frac{1}{2}\phi_2(1+\sin\frac{1}{2}\phi_2)}-\frac{4(1-\sin\frac{1}{2}\phi_2)S_2}{\sin\frac{1}{2}\phi_2(1+\sin\frac{1}{2}\phi_2)}\Big\}+\ldots.$$

which agrees with (19) the classical formula to first approximation. In view of (5) above, (20) shows that under relativity the scattering is proportional to:

(1) number of atoms per cc in the substance of the foil;

(2) thickness of the foil;

(3) the square of the nuclear charge.

The departures under the relativity law from the last two factors of proportionality noted in §11 are due to 2nd and higher powers in (16), the expansion of d^2. The relativity correction term is thus:

$$\Delta d^2=\frac{l^2}{V^2}\left[\frac{2(1-\sin\frac{1}{2}\phi)^2(2+\sin\frac{1}{2}\phi)}{\sin^2\frac{1}{2}\phi(1+\sin\frac{1}{2}\phi)}+\frac{4(1-\sin\frac{1}{2}\phi)S}{\sin\frac{1}{2}\phi(1+\sin\frac{1}{2}\phi)}\right]. \tag{21}$$

The effect which (21) has when added to (18) upon the reciprocal of the fourth power of the velocity of the particle, and the square of the cotangent of the half angle of deflection, will measure the relativity correction to these factors of proportionality in the scattering formula of Rutherford.

13. To make the study concrete and numerical, consider the scattering which would be effected by a film of gold foil, taking as constants:

for gold: $N=79$, $e=4.77\times10^{-10}$e.s.u., $c=3\times10^{10}$cm/sec.;

for α-particles: $E=2(4.77)\times10^{-10}$e.s.u., $M=4(1.63\times10^{-24})g$.

Hence: $l=NeE/c^2M=6.14\times10^{-15}$cm; $l^2=3.77\times10^{-29}$cm^2.

Graphs do not lend themselves readily to setting forth the difference between the results herein under relativity, and results under classical theory, because this difference is so minute. Hence the comparison is tabulated.

Table I shows for two different initial velocities of the α-particle how d varies with five representative half angles of deflection. The calculations are based upon formula (20) where the outside limiting angle is taken as $\frac{1}{2}\varphi_2=\frac{1}{2}\pi$ so that the d^2 is proportional to the total scattering for angles greater than those given in column I and the negative terms in the above formula are all zero.

Columns 2 and 5 of Table I give the correction by (21) which must be subtracted from the corresponding figure in column 3 or 6 to give

the d^2 according to Rutherford's formula. It will be noted that this difference is, with the single exception of the last figure in column 2, always less than one percent of d^2.

Columns 4 and 7 give a product which should be constant for all five angles when a given velocity is under consideration, according to the classical formula. Thus the departure of these figures from sameness is a kind of measure of difference in the two theories. It should be noted that these

TABLE I

Variation with ϕ

$\frac{1}{2}\phi$	$V=1/15=2(10)^9$ cm/sec. Δd^2	$d^2(10)^{24}$	$d^2\tan^2\frac{1}{2}\phi$	$V=1/30=10^9$ cm/sec. Δd^2	$d^2(10)^{24}$	$d^2\tan^2\frac{1}{2}\phi$
85°	$3.961(10)^{-21}$	.01465	$1.9136(10)^{-24}$	$1.5847(10)^{-20}$	.23435	$30.617(10)^{-24}$
60°	$6.648(10)^{-25}$	.63851	$1.9155(10)^{-24}$	$2.6590(10)^{-27}$	10.208	$30.625(10)^{-24}$
45°	$4.893(10)^{-27}$	1.9185	$1.9185(10)^{-24}$	$1.9574(10)^{-26}$	30.634	$30.634(10)^{-24}$
30°	$2.968(10)^{-26}$	5.7703	$1.9234(10)^{-24}$	$1.1872(10)^{-25}$	91.970	$30.657(10)^{-24}$
10°	$7.287(10)^{-25}$	62.273	$1.9361(10)^{-24}$	$2.9147(10)^{-24}$	987.60	$30.706(10)^{-24}$

TABLE II

Variation with V of $d^2V^4(10)^{-12}$

V	$\frac{1}{2}\phi=85°$	$\frac{1}{2}\phi=60°$	$\frac{1}{2}\phi=45°$	$\frac{1}{2}\phi=30°$	$\frac{1}{2}\phi=10°$
1/15	.23435	10.216	30.6958	92.325	996.37
3/15	.23451	10.2204	30.6767	92.268	994.05
2/15	.23435	10.2212	30.6556	92.088	990.56
1/30	.23435	10.208	30.6366	91.970	987.60

figures increase always with diminishing angle of deflection, although the amount of increase is never more than two per cent of the figure involved, when the angular range for $\frac{1}{2}\varphi$ is 75°. Geiger and Marsden used a column of figures similar to this last to set forth the results of their experiments upon scattering of α-particles by gold. Their experimental results showed an increase in the figures of constant column with diminishing angle of deflection, which meant that the scattering increased with diminishing angle of deflection at a greater rate than Rutherford's formula provided for. If the theory herein is correct, then part of this departure is accounted for by our results. However, the amount of this relativity departure from constancy in columns 4 and 7 is so minute compared with the experimental departures shown by Geiger and Marsden's data, that it would scarcely be considered an argument in favor of this theory.

14. In Table II for five different angles of deflection, the variation of d^2 with the initial velocity of the α-particle, is shown. The figures in columns 2 to 6 would be the same for each angle of deflection if d^2 varied inversely as the fourth power of the velocity. Thus the departure of the

figures in these columns from sameness is a measure of the difference between the relativity theory and the classical theory based upon the inverse square law of force. It will be noted that for the total range of velocity, from 2×10^9cm per sec. to 10^9cm per sec. representing ranges of something like 7 cm and 1 cm of air respectively for α-particles, the departure of these figures from constancy is less than one per cent, which is far too small to detect experimentally.

It thus appears that so far as the scattering of α-particles by gold and other metals is concerned, the facts are accounted for equally well by the relativity theory and the classical theory.

15. In this section we consider the scattering of H atoms after impact with α-particles, as effected by the relativity theory. This consideration gives entirely negative results. The reason for this is that we are obliged to confine ourselves to the study of effects in a 4-space due to a single gravitational center, and leave out of consideration effects due to two centers moving past each other, as was pointed out at the beginning of this paper. The theory of the scattering of H atoms by α-particles hangs upon the formula derived by Darwin[2] and based upon Newtonian mechanics

$$d=\tfrac{1}{2}b\tan\theta \qquad (22)$$

where d is the perpendicular distance from the H atom to the line of approach of the α-particle, and θ is the angle which the H atom after emerging from the collision with the α-particle, makes with the original line of approach of the α-particle, and b has the same significance as above. This expression for d is the same as (18) provided the asymptotic angle α is replaced by θ, though it describes a different physical situation. No such jump from our formula (16) for d^2 in terms of the asymptotic angle to a relativity formula analogous to (22) is justifiable since we cannot use Newtonian mechanics to help over the transition. If this step were possible then we could replace α in (16) by the angle of deflection of light atoms after collision with α-particles, and get a formula departing from that based on inverse square forces so slightly that it would not be detectable in a graph. It would thus not help at all to explain the very great departures from this law shown experimentally by the recent work of Rutherford, Chadwick and others. It is possible that when the gravitational potentials of a field due to two moving centers, are brought to light, that these experimental results may be partly explained as consequences of a relativity field of force, as well as the complex structure of the atoms involved in the collision.

UNIVERSITY OF MICHIGAN,
June 25, 1923.

THE HALL EFFECT AND SPECIFIC RESISTANCE OF CATHODICALLY DEPOSITED FILMS OF GOLD

By S. S. Mackeown

Abstract

Hall coefficient for sputtered films of gold was determined for films varying in thickness from about 10 mμ to 80 mμ, and was found to be independent of the current (even though current densities up to 10^6 amp./cm^2 were used), of the magnetic field (3 to 28 kilogauss), and of the thickness (computed from the surface density), and of previous treatment of the film, and to have the same value as for bulk metal, 643×10^{-6}. This is accurate to one per cent since the high current densities used gave e.m.fs. of over a milli-volt. The constancy of the coefficient agrees with the theory that the sputtered particles have individually the same properties as the bulk metal.

Specific resistance of sputtered films of gold is erratic for films less than 10 mμ thick, but for thicker films is proportional to $\rho/(\sigma-\sigma_0)$ where σ is surface density and ρ is the density. The specific resistance r came out about 3 times the value for bulk metal. The high value is doubtless due to poor electrical contact between particles. From the value of the constant σ_0, 20×10^{-6} gm/cm^2, the average size of the particles is of the order of 10^{-6} cm.

THE Hall effect of thin films has been studied by Kundt,[1] Moreau,[2] Wait,[3] and Steinberg.[4] Kundt used electrolytically deposited films of the ferro-magnetic metals. Moreau used chemically and electrolytically deposited films of silver and nickel. He found that the Hall coefficient varied with the thickness and explained his results on the transition layer theory suggested by Vincent.[5] Wait used chemically deposited films of silver, and found that the Hall coefficient was constant, independent of the thickness and had the same value as metal in bulk, for thicknesses as low as 23 mμ. Steinberg obtained his films by evaporation in a vacuum. In the case of silver and copper he found the Hall coefficient to be less than that for the bulk metals, and in the case of the iron films about five hundred per cent greater.

As far as is known, no previous attempt has been made to determine the Hall coefficient in the case of films obtained by cathodic sputtering.

[1] Kundt, Weid. Ann. **49**, 257, 1893
[2] Moreau, J. de Phys. **10**, 478, 1901
[3] Wait, Phys. Rev. **19**, 615, 1922
[4] Steinberg, Phys. Rev. **21**, 22, 1923
[5] Vincent, J. de Phys. **9**, 78, 1900

Apparatus and Procedure

The sputtering apparatus was of the usual form. The high potential was obtained by a half kilowatt 10,000 volt transformer, with a kenetron in series. The use of the kenetron eliminated the heating effect due to the reverse current, and allowed more rapid sputtering. The current was maintained at 15 milli-amperes. The vacuum was obtained with a rotary oil pump and a Gaede molecular pump in series. The pressure was measured on a McLeod gauge and the sputtering was all done at a pressure of about 30 μ, the residual gas being air.

The films were deposited on square glass plates that were approximately 12 cm on a side. The cathode was a square piece of commercially pure gold 12 cm on a side. The terminals were first deposited by sputtering dense films of gold as shown in Fig. 1a. The mask used to protect the rest of the film is shown in Fig. 1b. The film to be studied was then

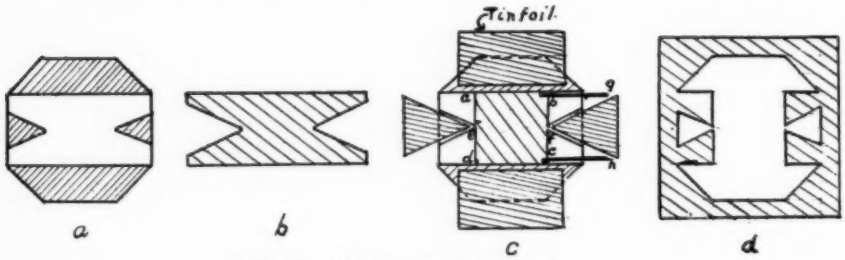

Fig. 1. Shields used in sputtering.

deposited so as to overlap the terminals. The film used in studying the Hall effect, is indicated as *abcd*, in Fig. 1c. It was square, 7 cm on a side. The mask used in sputtering this film is shown in Fig. 1d. Contact to all four terminals was made by cementing thereon tin foil with "Clamping Paste," kindly furnished by the General Electric Company. A spectrophotometric test showed no difference in uniformity of the deposit. The film, ready for mounting, is shown in Fig. 1c. Additional terminals were connected to the top and bottom of the film (*g* and *h* in Fig. 1c) in order to measure the resistance by the potentiometer method, thus eliminating any error due to poor or variable contacts. The side terminals *e* and *f* were adjusted by scraping with a knife so that they were at the same potential when current was flowing through the film and no magnetic field was present.

In the case of film as thin as those used in this study, the term thickness loses its usual meaning, and it seems desirable to speak of mass per square centimeter, which will be called "surface density" hereafter. Both the Hall coefficient and the specific resistance can be expressed as signifi-

cantly and as clearly in terms of this surface density as of thickness. In order, however, to enable comparison with other work, the term thickness will be used in places, and it should be understood that it is used in the sense of average thickness, and is determined by dividing the mass per square centimeter by the density of gold in bulk, taken to be 19. The films studied varied in thickness from approximately 10 mμ to 80 mμ.

The surface density of these films was determined in the following manner. Thin sheets of mica, having an area of about 40 cm^2 were weighed on an assay balance, sensitive to .01 mg, before and after sputtering. A piece of glass, similar to those on which all the films were deposited was placed beside the mica in the sputtering jar during the sputtering and received, presumably, the same thickness of film as the mica. The transmission of blue light, ($\lambda = 5000$ A), by both the film on the glass and that on the mica were then measured with a spectrophotometer.

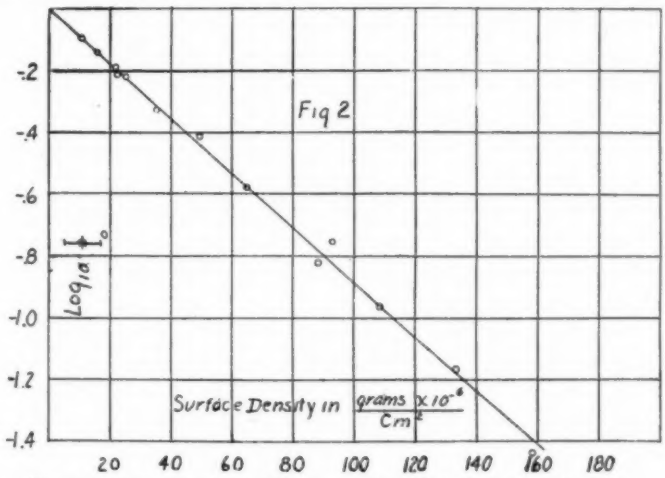

Fig. 2. Transmission of light as a function of surface density.

Since the transmission of this same frequency was determined before sputtering for both the glass and mica, the intensity of the incident light could be corrected for the light reflected or absorbed by the glass and mica. On making this correction concordant values for the transmission of the two films were obtained in each case. For a series of such films of varying thickness, it was found that if the logarithm of the ratio of the light transmitted to the incident light (log I/I_0) was plotted against surface density, a straight line going through the origin was obtained. This curve is plotted in Fig. 2. By measuring the intensity of light transmitted by the films used in determining the Hall coefficient, correcting for the loss of light due to reflection from the glass surface which was found to be eight per cent, the surface density of these films could be readily determined from the curve.

This curve is not corrected for the difference in the reflecting power between a glass-air and glass-gold surface. This will not affect the accuracy of the determination of the surface density, since the same procedure was used in determining the curve as in using it to obtain the surface density.

The Hall electromotive force was measured by a potentiometer. Current was sent through the film only while a balance was being made. A number of readings of the potentiometer were taken for each value of the resistance, in order to minimize any thermal electromotive forces and any differences in potential between the side terminals due to changes in the resistance of the film from heating. Sufficient resistance was kept in series with the film so that any change of its resistance due to heating would not affect the value of the current to any appreciable extent. By taking these precautions, it was possible to use large values for the current, with a resulting increase in accuracy in measuring the Hall electromotive force. In measuring the Hall effect the film was mounted rigidly in a suitable wooden frame, attached to one of the pole pieces of the magnet.

The magnet used was made by the Société Genevoise and was water cooled. In most cases the pole pieces were cylinders 10 cm in diameter, and these were kept at a distance of 0.9 cm apart in order to obtain as uniform a field as possible. The value of the field was determined by a flip coil and a standard mutual inductance in series. The current in the primary of the mutual inductance was adjusted until the same throw of a ballistic galvanometer was obtained on breaking this current as by removing the flip coil from the field. The ballistic galvanometer was used simply as an indicating device and its constants did not enter into the computations of the field strength.

Experimental Results

Hall Effect. The Hall coefficient was found to be independent of the current, magnetic field strength, and thickness in all the films studied. The Hall electromotive force E is usually represented by the formula

$$E = RHI/t$$

where R is the Hall coefficient H the magnetic field strength, I the current, and t the thickness. If surface density is used in place of thickness,

$$E = R'HI/\sigma$$

where σ is the surface density, and $R' = R\rho$ where ρ is the density of the metal.

The proportionality between the Hall electromotive force and the current is shown in Fig. 3. This proportionality was found to hold for very large current densities. On account of the large surface for radia-

tion, it was possible to use current densities as high as 10^6 amp. per cm.^{2} These results would indicate that the Hall coefficient is independent of the current, and does not show any saturation effect. On account of the extreme thinness and the large current densities, the Hall electromotive

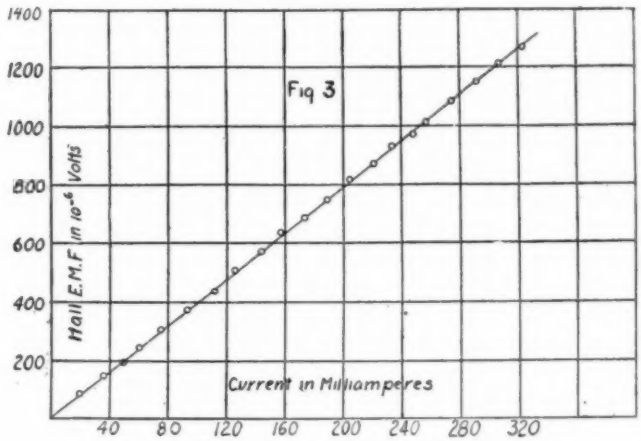

Fig. 3. Hall e.m.f. as a function of current.

force is very much greater than can be obtained in metal in bulk, and the accuracy of measuring it is consequently much greater.

The proportionality between the Hall electromotive force and the magnetic field strength is shown in Fig. 4. This curve is for a film having

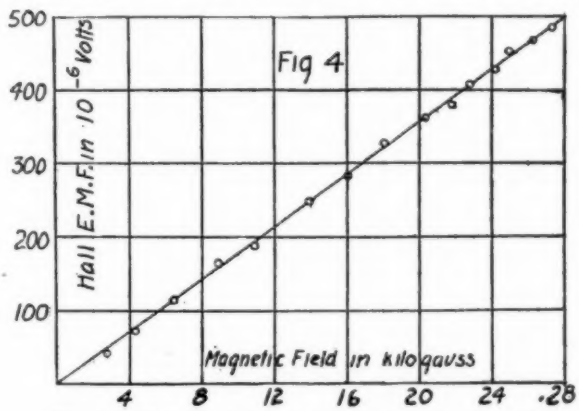

Fig. 4. Hall e.m.f. as a function of magnetic field.

an area of about 6 cm^2 and smaller pole pieces were used in order to investigate the effect at high values of the field strength. No difficulty was experienced in measuring the Hall electromotive force for field strengths ranging from about 3 to 28 kilogauss.

The relation between the Hall electromotive force and surface density was determined for films having an average thickness ranging from about

10 mμ to 80 mμ. Curve 1 in Fig. 5 shows the Hall electromotive force plotted against the reciprocal of surface density. This curve represents an average of practically all the measurements of the Hall effect. The values of E/HI plotted as ordinates were determined from the slopes of curves similar to that shown in Fig. 3, and each point represents the average of a great number of readings taken at different values of the current and field strength. The ordinates of this curve are in c.g.s. units. If we assume an average value of 19 for the density of the films,

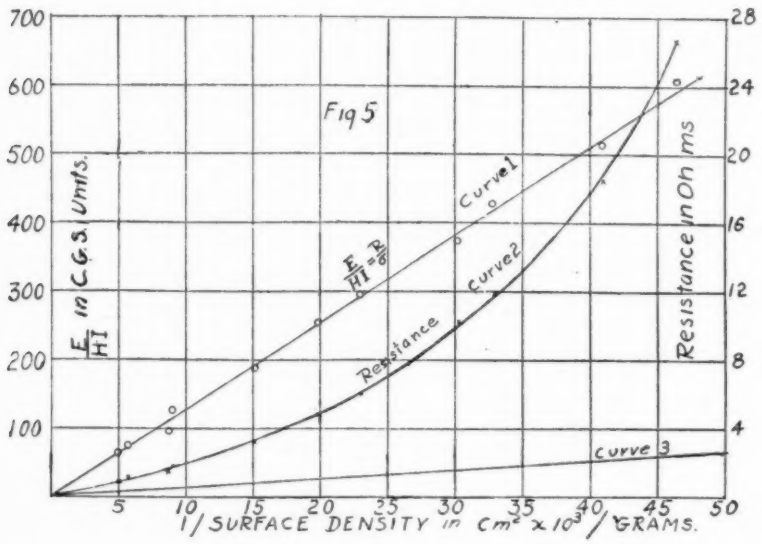

Fig. 5

Curve 1: Hall e.m.f. divided by HI as function of reciprocal of surface density.
Curve 2: Resistance of films.
Curve 3: Resistance of bulk metal.

the value of the Hall coefficient, expressed in terms of the thickness, determined from this curve is 643×10^{-6}. The value of the Hall coefficient determined for the bulk metal ranges from 570×10^{-6} to 710×10^{-6}.

The Hall coefficient was found to be independent of the previous history of the films. Measurements made directly after sputtering gave the same value for the Hall coefficient as measurements made after heat treatment and also as measurements made after the films had stood for two months exposed to the air. In fact, the Hall coefficient was not changed by any treatment that did not noticeably injure the film. This is in marked contrast to the behavior of the resistance of these films and also to the change of resistance in a magnetic field in the case of bismuth films.[6]

[6] Curtis, Phys. Rev. **18**, 255, 1921

It is well known that the resistance of sputtered gold films increases enormously for thicknesses less than about 10 mμ.[7] Attempts to obtain reliable data on the Hall effect with these very thin films were not successful on account of the large change in resistance of the films during measurement. The potential between the side terminals would change so much that the relatively small change due to the Hall effect was masked. This is evidently due to the fact that the resistance of the films changed as current was sent through them, and the resistance did not change uniformly all over the surface. Although these films appeared uniform to the eye, the points of equipotentials on the two sides, when current was sent through the film with no magnetic field present, was not, in general, at the midpoints of the two sides, and the location of these points of equipotential seemed to change every time current was sent through the film. Another difficulty in measuring the Hall effect of these very thin films is that as the resistance is very high, only a small current could be sent through the films without unduly heating them. Consequently the magnitude of the Hall electromotive force was greatly reduced. From such data as could be obtained, however, no evidence was obtained that the Hall coefficient changes for these films, although the specific resistance increases to several hundred fold its value for bulk metal.

Specific resistance. The resistance and the change in resistance in sputtered films has been studied by many observers, among whom may be mentioned Miss Stone,[8] Patterson,[9] Swann,[10] Pogeny,[7] King,[11] and Koller.[12] The results of the present work are in agreement with the results previously reported. Values for the resistance of films less than 10 mμ will not be included in this report, for the resistance is so unstable for these very thin films that elaborate precautions are necessary to make the data trustworthy, and these precautions were not taken. The value of the resistance of those films on which the Hall effect was studied is given, as the resistance of these films after aging at 150°C for two hours is quite constant. Over a long period of time, however, the resistance of these films would change by several per cent. The curve between the resistance and the reciprocal of the surface density is shown in Fig. 5, Curve 2. Curve 3 is the curve that would have been obtained if the specific resistance of the films had been constant and had had the same value as that for gold in bulk.

[7] Pogeny, Phys. Zeit. **15**, 563, 1914
[8] Miss Stone, Phys. Rev. **6**, 1, 1899
[9] Patterson, Phil. Mag. **4**, 652, 1902
[10] Swann, Phil. Mag. **28**, 467, 1914
[11] King, Phys. Rev. **10**, 291, 1917
[12] Koller, Phys. Rev. **18**, 221, 1921

Discussion of Results

The work of Smith,[13] Wold,[14] Lebret,[15] and others would indicate that the Hall coefficient depends, at least in part, on the crystal structure of the metals. Wait[3] has shown that the Hall coefficient should be the same for films consisting of groups of crystals as for the metal in bulk, even though these particles are not in as intimate electrical contact as in the bulk form. The results of this study seem to confirm the theory that these films consist of particles of the same crystal structure as that obtaining in the bulk form.[16] The films will therefore be considered as consisting of particles, or small crystals, which have, individually, the same properties as the bulk metal, arranged at random on the surface of the glass.

When the surface of the glass is only partly covered by these particles, there are individual particles as well as groups of particles that do not make electrical contact with the other particles deposited. In this state the addition of a relatively few particles may decrease the resistance greatly as they may serve to establish electrical contact between large groups of particles. The resistance would be a complicated function of the number, size and physical condition of the particles.[17] Under these conditions, the resistance would be unstable since contacts might easily be made and broken between groups of these particles by heat. Since the resistance of the films used in this study was practically constant, it is probable that the surface is practically covered and that all the particles are in electrical contact. It is interesting to consider how the resistance, or preferably the conductivity, will depend on the number of particles deposited, when the surface is practically covered.

Consider a film in this state. All the particles are touching other particles. If the particles have fallen at random, according to the law of probability, the surface is not covered to a uniform depth and all the particles will not be equally effective in conducting an electric current. If now an additional number of particles ΔN are added, the additional number of particles that will be made effective in conducting the current will be ΔN, since the contour of the surface will, on the average be the same.

If K is the conductivity,

$$dK = k_1 dN$$
$$K = k_1(N - N_0)$$

[13] Smith, Phys. Rev. **10**, 358, 1917; Phys. Rev. 17, **37**, 1921.
[14] Wold, Phys. Rev. **7**, 169, 1916
[15] Lebret, Leid. Com. 119, 1895.
[16] Kahler, Phys. Rev. **17**, 210, 1921
[17] Koller, loc. cit.[12]

where N_0 is the equivalent number of particles that are ineffective in conducting the current due to the roughness of the surface. Since the number of particles is proportional to the mass per square centimeter

$$K = k(\sigma - \sigma_0)$$

In Fig. 6, the conductivity is plotted against the surface density, and it is seen that the above equation is satisfied by the data, except at small values of the surface densities. Actually the curve is as shown and joins the x axis at a surface density of about 6×10^{-6} grams per square centimeter. The value of the constant k gives the specific conductivity

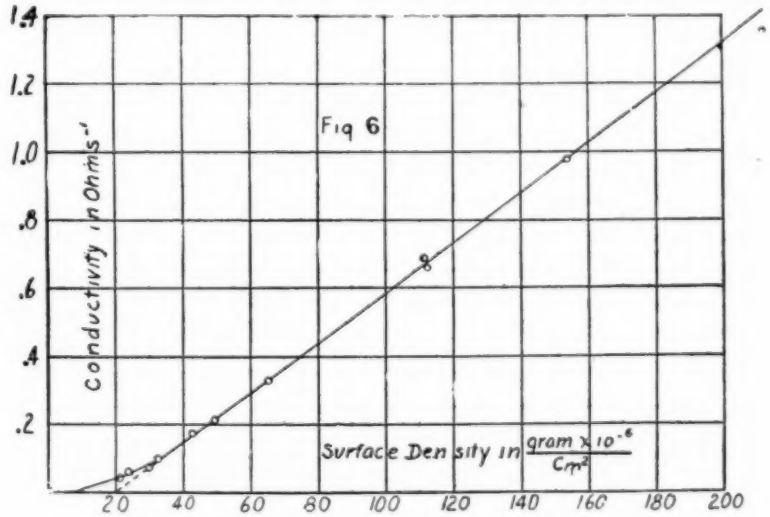

Fig. 6. Conductivity as a function of surface density.

in terms of grams per square centimeter. This is about .35 of the value of the specific conductivity for gold in bulk. This difference is probably due to the gas absorbed by each particle which prevents the particles from making good electrical contact.[18]

From this curve between the conductivity and the surface density it is possible to obtain a rough approximation of the size of the particles. If we assume that the particles are all the same size, the intercept on the x-axis can be shown to be equal to the surface density of a single layer of particles, completely covering the surface. Dividing 20×10^{-6} by the density of gold 19 we get 10^{-6} cm as the average thickness of the particles.

In conclusion the writer wishes to express his thanks to Professor F. K. Richtmyer for his constant help and encouragement throughout the work.

CORNELL UNIVERSITY,
August 7, 1923

[18] Kohler, loc. cit.[12]

FREE CONVECTION OF HEAT IN LIQUIDS

By Roy A. Nelson

Abstract

Free convection of heat from a hot wire in various liquids.—(1) *Photographic study of the convection streams.* Both a parallel ray and a schlieren method were used and gave similar results. Photographs are reproduced for water, olive oil and glycerine. In all cases there is a necking down of the stream a few millimeters above the wire. When the wire is first heated, a layer of liquid all around the wire is heated; the lower half first moves down, then stops and goes up joining the stream which follows the upper half, which had proceeded as a distinct semi-circular pulse. The appearance of the image of the wire tends to confirm Langmuir's suggestion of a stationary film on the surface. Bubbles on the wire in olive oil were observed to execute interesting oscillations. (2) *Variation of heat loss with the excess temperature of the wire over that of the liquid.* After the wire (a silver one, .33 mm in diameter) had been heated electrically for about 10 minutes a steady state was reached; then the resistance of the wire was measured and the mean temperature of the liquid was determined with a mercury thermometer. It was found in the case of water, alcohol, CCl_4, glycerine and castor oil, that the heat loss per cm² per sec. is equal to $b\theta^n$ when n has the values 1.15, 1.105, 1.125, 1.25 and 1.24 respectively. The measurements of A. H. Davis are shown to give values of n of about 1.15 for five liquids, but there is an indication that n depends upon the diameter of the wire. The factor b varies with the liquid and the mean temperature and also perhaps with the diameter of wire.

Part I. Photographic Study

OF THE large amount of work that has been done on convection of heat, practically all has been from the viewpoint of the rate of loss from heated bodies and the effect of the physical properties of the fluid on this rate. Very little has been done on the motions and conditions that exist in the fluid due to convection currents.

Pramanik[1] has made an optical study of free and forced convection from hot wires in air. He gives a number of photographs showing the convection currents, both when the currents are gravity currents and when a stream of air is forced past the wire. He also shows the effect of having several heated wires close together.

In the present work, which was begun before Pramanik's work appeared, a large number of photographs have been taken, showing the convection currents in liquids of widely different physical properties.

[1] Pramanik, Proc. Indian Assoc. Cult. Sci. **7**, 115, 1922

1. *Methods of obtaining photographs.* Since the index of refraction of a liquid changes with the density, it is not difficult to make the convection currents in liquids visible and to photograph them.

In this work two methods were used to obtain the photographs; the "parallel light" method, and the "method of striae" or a modification of the Schlieren Method.

The first method is shown in upper part of Fig. 1. An arc light D was placed at the focus of the lens L_1 so that a parallel beam of light passed through the box with the glass sides containing the liquid. The box was 7.5 cm by 8 cm, and 10 cm high. The heating element was a manganin wire 2.7 cm long and 0.0315 cm in diameter. L_2 and L_3 were camera lenses and a magnification of from 3 to 4 diameters was used in obtaining the photographs.

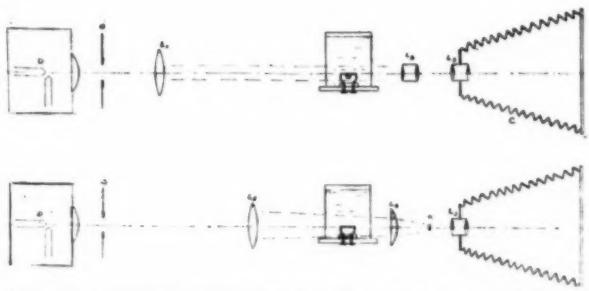

Fig. 1. Optical arrangements; parallel light method above; method of striae below.

In the second method, also shown in Fig. I, a long focus lens L_5 was placed so that a converging beam of light passed through the liquid along the axis of the heating wire. To shorten the distance between the camera and the wire so a magnification could be obtained, a lens L_4 was used to cause the beam to converge rapidly after passing through the liquid. A steel hemisphere K, 0.47 cm in diameter was placed so that practically all the light was shut off from the camera when the liquid was all at the same temperature. When the heating current was established, the liquid in the neighborhood of the wire was heated and moved upward. The difference in the densities of different parts of the liquid caused the light to be bent around the obstacle K and an image was formed on the plate in the camera.

In order to compare the two methods for showing the convection streams, photographs were taken of convection streams under almost the same conditions. The photograph in Fig. 2a was taken by the parallel light method and Fig. 2b by the method of striae, the magnifications being about 5 times and 3.5 times respectively. The same general characteristics may be seen in both photographs. The parallel light method

Figures 2,3 and 4. Water.

2a. Parallel light. 2b. Method of striae.

3a. h = 1.2; 3b. h = 3.7; 3c. h = 6.9

4a. After $\frac{1}{2}$ sec.; 4b. 1 sec.; 4c. $1\frac{1}{2}$ sec.

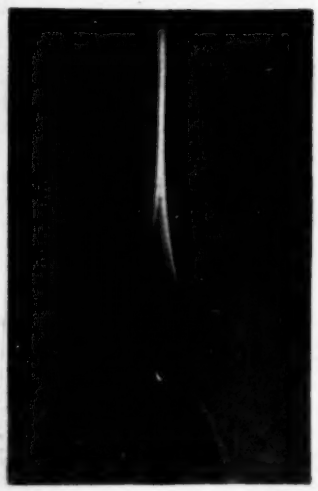

Fig. 5. Olive oil

Fig. 6. Glycerine

Convection streams in water, olive oil and glycerine
Fig. 2. Comparison of two photographic methods; water
Fig. 3. Variation with heat loss h, in cal. per cm^2 per sec.
Fig. 4. Variation with time after starting the current.

shows the convection streams at a greater distance above the wire because a larger region was illuminated in using this method. Photographs taken using the schlieren method were found to show more details of the convection stream near the wire and so this method was used when the convection flow near the wire was studied. The stream of rising fluid acts as a lens for the beam of light passing through it. This was shown by changing the position of the lens L_2 in Fig. 1. The convection stream could be made to appear bright as shown in the photographs or, if the lens L_2 was moved farther from the box the image would be dark with a bright edge.

If the glass box was turned so that the light passed through the liquid perpendicular to the axis of the wire, it was found that the image of the wire could be made much larger when the heating current was on than when it was off. If the lens L_2 was moved toward the wire a position could be found where the image of the wire practically disappeared when the heating current was turned on. This spreading out of image of the wire seemed to be the same above the wire as it was below. This is what would happen if Langmuir's theory that there is a stationary film on a heated surface is true for liquids. The spreading of the image would not be the same below the wire as it is above if the liquid film was not stationary but was being constantly replaced by unheated liquid. Some of the photographs which will be discussed later on also tend to confirm this theory.

2. *Convection currents in water.* In water it was found that it was necessary with the size wire used to have a rate of heat loss of at least 0.8 calories per cm^2 per sec. in order that convection streams would be visible. Figs. 3a, 3b, and 3c show photographs taken of water having heat losses of 1.28, 3.71, 6.86 cal per cm^2 per sec., respectively. The distances between the horizontal lines of the photographs represent distances of one centimeter. The photographs show that at a short distance above the wire the width of the convection streams is the largest. This is no doubt due to the heated liquid coming out from below the wire. But at a short distance farther up the stream narrows down and is very sharp. Then as it proceeds up it begins to diffuse out into the cooler liquid. It is interesting to note that there is a region in which the flow is practically linear. Figs. 3b and 3c show this quite distinctly.

Figs. 4a, 4b, 4c show the formation of the convection stream. These photographs were taken, using the method of striae. The heat loss in these four cases was all the same, 6.7 cal per cm^2 per sec, but they were taken at $\frac{1}{2}$, 1 and 1.5 sec., respectively, after the current was turned on. Fig. 4a shows the heated layer close to the wire and the distance moved upward is very small. From visual observation, the beginning of the

convection flow had the appearance of a wave moving outward from the wire, but when the lower half had proceeded a short distance down it was reflected and moved upward. Fig. 4b shows this wave moving up. The central dark spot represents the position of the wire. Fig. 4c shows the wave which proceeds upward. The wave could be seen until it reached the surface of the water. These photographs all seem to substantiate Langmuir's film theory. If the molecules of the liquid received heat only as they came in contact or very close to the wire, the heated liquid would not be seen at the lower side of the wire.

If the box was turned so the light passed through the liquid at right angles to the axis of the wire and the current was turned on, the wave shown in the previous photographs appeared as a "wave front" moving upward. Over the central portion of the wire this "wave front" was straight unless there was some disturbing condition such as bubbles or particles clinging to the wire. Above the ends of the wire the end effect could be seen and the "wave front" was seen to curve downward.

3. *Convection currents in alcohol.* Using alcohol as the convecting liquid, the same general characteristics were observed. The stream does not converge as sharply as in the case of water but convection currents for a lower rate of heat loss could be made visible. The velocity of the initial wave which travels up is higher than in water because of the lower viscosity. It was noticed in alcohol and not in the other liquids tried, that near the surface the bright image had a tendency to move slowly back and forth, even when the liquid as a whole seemed perfectly quiet.

4. *Convection currents in olive oil and glycerine.* Fig. 5 shows the stream lines in olive oil after the heat current had been on for fifteen minutes and a steady state had been reached. When the heating current was first turned on a wave of the same nature as shown in Fig. 4 moved slowly upward.

Fig. 6 shows the same effect in glycerine. This photograph was taken 25 minutes after the heating current was turned on.

An interesting phenomenon was observed in olive oil with the light passing through the box perpendicular to the wire. When the wire was heated so that bubbles formed on the wire, these bubbles would move back and forth along the wire. If there was only one bubble it would vibrate over nearly the entire length of the wire. If there was more than one bubble, they would oscillate back and forth, rebounding when two came close to each other. After some time the bubble would come to rest. When the heating current was turned off the bubbles would rise to the surface. This same phenomena was observed in glycerine but the oscillatory motion was damped out much quicker.

Another point of interest in this connection was that if bubbles were formed when the heating current was turned on, and if after the wave like that shown in Fig. 4c had proceeded a centimeter or two above the wire the switch was opened, the bubbles would rise rapidly until they reached this wave and then rise to the surface with it, but would not pass through the wave.

Part II. Measurements of Heat Losses From a Wire

The first experimental study of free convection seems to have been made by Dulong and Petit.[2] They studied the rate of loss of heat from thermometer bulbs in gases maintained at a constant temperature. They found that the rate of loss of heat by convection was proportional to $\theta^{1.233}$ where θ represents the excess in temperature of the heated body over that of the gas.

Lorenz[3] solved mathematically the case for the rate of heat loss from a vertical plate by making certain assumptions regarding the air currents

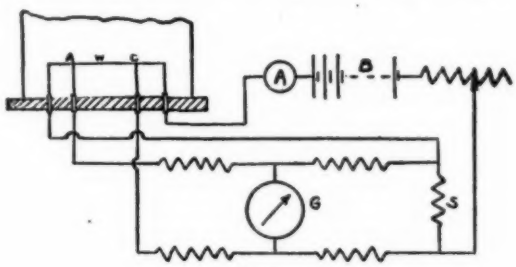

Fig. 7

near the plate. He found that the rate of heat loss should be proportional to $\theta^{5/4}$. This has been verified by experiments on small vertical plates by Langmuir,[4] and on large vertical plates at the National Physical Laboratory of Great Britain.[5] Langmuir[6] has also shown that for heated wires in gases the same exponent of θ holds for temperatures up to 600°C.

The present investigation was undertaken to determine whether the variation of convection with the temperature excess for liquids follows a simple law such as that for gases: $h = b\theta^n$.

1. *Experimental methods.* The apparatus used is shown diagrammatically in Fig. 7. The heating wire was of silver and was 0.033 cm in

[2] Dulong and Petit, Ann. de Chim. et Phys. **7**, 1817

[3] Lorenz, Ann. der Phys. **13**, 582, 1881

[4] Langmuir, Trans. Amer. Electrochem. Soc. **23**, 299, 1913

[5] Report on "Heat Transmission by Convection and Radiation" published by the Food Investigation Board.

[6] Langmuir, Phys. Rev. **34**, 401, 1912

diameter and 16.9 cm in length. The liquid under investigation was contained in a glass box 25 cm by 10 cm by 12 cm. The temperature of the wire was determined by measurements of its resistance, using a Kelvin Double Bridge. The potential drop leads were silver wires 0.015 cm in diameter and soldered to the heating wire 2.2 cm from the ends. The temperature coefficient of the heating wire was found to be 0.0388. The potential drop over the 0.01 ohm resistance S was compared with that of the silver wire. The heating current was taken from a set of storage batteries having a large capacity, the current thus being maintained amply constant.

From preliminary experiments it was found that the temperature of the wire increased rather rapidly when the heating current was first turned on, while after the current had run for about 10 minutes the change in temperature of the wire was proportional to the time and corresponded to the rise in temperature of the liquid as a whole. In taking the readings the heating current was allowed to run until this steady state had been reached; then the resistance was measured and the liquid stirred; then the mean temperature of the liquid was determined with a mercury thermometer.

2. *Results of experiments.* The liquids used in the experiments were water, alcohol, carbon tetrachloride, glycerine and castor oil. These liquids differ greatly in their physical properties and especially in regard to viscosity. In Table I the constants for these liquids are given. The values given in the table were principally taken from the 7th Edition of the Smithsonian Physical Tables and from Landolt-Börnstein "Physikalisch-Chemisch Tabellen."

TABLE I

Physical constants of liquids studied

Liquid	ρ	η	c	k (10)^4	α (10)^4
Alcohol	0.792	0.011	0.46	4.3	11.0
Toluene	0.866	0.005	0.34	3.1	10.9
Aniline	1.023	0.045	0.53	4.1	8.5
CCl_4	1.582	0.0097	0.31	2.5	2.66
Water	1.000	0.0101	1.00	14.0	3.0
Olive oil	0.916	0.989	0.43	3.9	3.9
Glycerine	1.26	8.5	0.73	7.0	6.8
Castor oil	0.969	7.91	0.42	4.2	

ρ = density $\quad$ η = viscosity $\quad$ c = specific heat per unit vol.
k = thermal expansion $\quad$ α = coefficient of cubical expansion

In Table II the results of a representative set of readings for water are given. The current through the wire and the resistance are given in the first two columns, the heat loss in calories per cm^2 per sec. h, is given in the third column. θ is the temperature difference between the wire and

the liquid, i.e., $\theta = t_W - t_L$. The value of the exponent n in the equation $h = b\theta^n$ was obtained by plotting the logarithms of h and θ and determining the slope of the lines. The ratio h/θ^n is given in the last column.

TABLE II

Water *Mean temperature 24.8°C* $n = 1.147$

I	R	h	t_W	t_L	θ	θ^n	h/θ^n
4.91	.026030	0.1151	26.28	24.36	1.94	2.143	.0537
8.33	.026312	0.3354	29.30	23.34	4.96	6.276	.0535
12.85	.026866	0.8147	35.34	24.46	10.88	15.45	.0528
15.86	.027397	1.266	41.10	24.86	16.24	24.47	.0517
20.88	.028392	2.273	51.97	25.75	26.19	42.33	.0537
26.40	.029946	3.833	68.94	27.97	40.97	70.71	.0542

The results obtained for the different liquids used are collected in Table III.

TABLE III

Liquid	t	n	h/θ^n	Liquid	t	n	h/θ^n
water	10°C	1.156	.0422	CCl_4	18°C	1.131	.0133
water	19	1.165	.0458	CCl_4	22	1.117	.0144
water	24	1.147	.0525	glycerine	19	1.244	.0099
water	25	1.147	.0533	glycerine	27.5	1.247	.0112
water	32	1.141	.0582	castor oil	6.5	1.26	.00442
alcohol	20	1.105	.0212	castor oil	18.0	1.21	.00601
alcohol	20.5	1.105	.0216	castor oil	34.0	1.27	.00589

A. H. Davis[7] gives values for the relation between the rate of heat loss and the temperature difference. He used a Wheatstone bridge method of measuring the resistance of the heated wire and by compensating leads corrected for the end effects. He assumed that the heat loss per unit length was proportional to θ^2 but his table shows that the ratio H/θ^2 was far from constant.

In Table IV the results given by Davis have been recalculated by the present writer and the value of the exponent n determined for each liquid. The heat loss is expressed in calories per cm² per sec. instead of calories per cm length per sec. as in his table.

The results show that the values of the exponent n should be between 1 and 1.25 instead of the value $n = 2$ assumed by Davis.

From the present writers' experiments, therefore, and from the present examination of Davis' measurements, it appears that the rate of loss of heat is not proportional to θ^2 but to θ^n where n has a value somewhat greater than unity. For all liquids tried except glycerine and castor oil, the value of n is not far from 1.15. In using liquids of high viscosity it was very difficult to obtain steady readings and in plotting the graph

[7] A. H. Davis, Phil. Mag. **44**, 933, 1922

from the logarithms of h and θ, it was found that the points were more scattered for glycerine and castor oil than for the other liquids. Davis states that his results for glycerine were the least satisfactory. This may account for the difference between the values of n for glycerine obtained from Davis' results and from those of the present writer.

TABLE IV

Values of h/θ^n, where h = heat loss in cal/cm and θ = excess temperature
(Calculated by the present writer from A. H. Davis' measurements)

Liquid	wire diameter	n	1	2	5	10	20	50
Toluene	0.0083	1.111		.0305	.0305	.0308	.0305	.0307
	0.0155	1.154	.0202	.0198	.0194	.0196	.0199	.0204
CCl_4	0.0083	1.127	.0242	.0238	.0241	.0240	.0241	.0240
	0.0155	1.157	.0166	.0168	.0163	.0167	.0166	.0166
Aniline	0.0083	1.173	.0274	.0286	.0277	.0278	.0276	.0285
	0.0155	1.167	.0205	.0201	.0196	.0197	.0202	.0207
Glycerine	0.0083	1.000		.0368	.0360	.0368	.0395	
	0.0155	1.152		.0183	.0172	.0171	.0176	.0183
Olive oil	0.0083	1.146		.0184	.0185	.0183	.0183	.0186
	0.0155	1.173		.0124	.0118	.0120	.0121	.0125

In Tables III and IV the values of the ratio h/θ^n are not constant but vary with the liquid, the mean temperature of the liquid and probably with the size of the heating wire. However, no definite conclusion can be drawn from the change in the ratio h/θ^n with the wire diameter from Table IV, because the mean temperatures of the liquids were not given by Davis. The value of the exponent n is nearly the same for the different liquids and does not change much when the temperature of the liquid is changed. There is an indication from Table IV that the value of n changes with the size of the heating wire, but the accuracy of the measurements is not sufficient to show definitely whether or not this is true. Since n is nearly the same for liquids of widely different physical properties, it is evident that the value of the coefficient b must be the predominating factor in determining the free convection of heat by a liquid.

It is planned to carry out further investigation on the loss of heat by convection in other liquids and determine the effect of the size of heating wire on the value of the coefficient b and on the value of the exponent n. If it is found that the value of the coefficient b is independent of the diameter of the wire, then this coefficient may be taken as a measure of the convective cooling power of a liquid. Even if b is a function of the diameter of the wire, the relative cooling power of different liquids may be found by comparing the values of b when determined with the same size

heating wire. It may also be possible to express b as function of the physical properties of the liquid but so far no simple relationship has been found.

Rayleigh[8] suggests the possibility of applying the principle of similitude to the problem of convection of heat. Richardson[9] and Davis[10] have applied this method and obtained relations for the rate of loss of heat from similar bodies immersed in viscous fluids. Davis has shown that the grouping of variables given by the principle of similitude gives satisfactory results for convection in gas, carbon tetrachloride, aniline, toulene, olive oil and glycerine. He also shows that the thermal conductivity of the liquid should be the predominating physical property in facilitating cooling by convection. The values of the ratio h/θ^n given in Table III bear out this statement, since water has the highest thermal conductivity and also gives the largest value for the ratio h/θ^n.

In a recent paper, Rice[11] has applied Langmuir's film theory and dimensional reasoning to obtain equations for free and forced convection in a liquid. He has used free convection as a method of determining the thermal conductivities of toluene, glycerine, olive oil, aniline, carbon tetrachloride and No. 12 transil oil.

The writer wishes to acknowledge his indebtedness to Professor A. P. Carman for the interest in and the suggestions made in the course of this investigation.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS,
June, 1923.[12]

[8] Rayleigh, Nature, **45**, 66, 1915
[9] Richardson, Proc. Phys. Soc., May 1920
[10] Davis, Phil. Mag. **40**, 692, 1920; **44**, 329, and 928, 1922
[11] Rice, (Abstract) Phys. Rev. **21**, 474, Apr. 1923
[12] Received July 14, 1923

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE CHICAGO MEETING, NOVEMBER 30 AND DECEMBER 1, 1923

The 123rd regular meeting of the American Physical Society was held at the University of Chicago on Friday and Saturday, November 30 and December 1, 1923. There were morning and afternoon sessions on both days with an average attendance of about 250. The presiding officer was Professor C. E. Mendenhall, President of the Society.

Professor Niels Bohr was elected an honorary member at the meeting of the Council held on Friday, November 30. On Saturday morning Professor Bohr addressed the Society on "The Quantum Theory of Atoms with Several Electrons." This address was attended by about 350 persons.

On Friday evening an informal dinner of the Society was held at the Quadrangle Club, attended by about 100 persons.

The regular meeting of the Council was held on Friday evening at the Quadrangle Club. The following were elected to membership: William H. Adamson, William P. Allis, Francis J. Altman, Emmett C. Bailey, Kendall Banning, Henry A. Barton, Harry C. Bates, Alva H. Bennett, Fred T. Bowditch, Arnold E. Bowen, Edward L. Bowles, Milton L. Braun, Nathanael P. Breslauer, Frank W. Bubb, G. Howard Carragan, John A. Carroll, C. T. Chu, Gyfford D. Collins, William R. Cullen, George E. Davis, S. S. DeVinney, Herbert N. Eaton, Carl H. Eckart, Emanuel Feit, Erwin W. Felkel, Irwin H. Fenn, Walter F. C. Ferguson, William G. H. Finch, Donald D. Foster, Edward E. Free, R. H. George, Glenn W. Giddings, L. P. Granath, John J. Grebe, Wayne B. Hales, Vincent C. Hall, Glenn B. Harvin, Charles C. Hatley, Cedric E. Hesthal, Harry Hill, O. J. Hodge, John J. Hopfield, William V. Houston, Henry D. Hubbard, Simon H. Ingberg, M. F. Jameson, Ralph S. Jessup, Roy Kegerreis, Carleton V. Kent, William S. Kimball, S. M. Kintner, Edward B. Kirk, H. P. Knauss, Frank C. Kracek, Bernhard Kurrelmeyer, Quick Landis, E. O. Lawrence, Robert B. Lindsay, Edward J. Lorenz, Donald

H. Loughridge, John P. Magnusson, William A. Mann, L. J. McBane, Harry J. McNicholas, Atherton H. Mears, Wilmot V. Metcalf, J. Franklin Meyer, R. F. Miller, J. C. Morris, Jr., Roger M. Morrow, Warren W. Nicholas, Walter M. Nielsen, John T. Norton, Julius Olsen, Vincent Pagliarulo, C. S. Pettis, Francis P. Phelps, Robert J. Piersol, Howard A. Pritchard, E. J. W. Ragsdale, Henry S. Rawdon, H. J. E. Reid, K. E. Rollefson, C. Fred Sacia, Walter A. Schneider, E. H. Schrieber, H. E. Seemann, Jerry H. Service, G. M. Shrum, Raymond L. Steinberger, Charles F. Stoddard, F. J. Studer, George F. A. Stutz, Jr., Walter F. Stutz, M. Sussman, Tracy Y. Thomas, Robert A. Thornton, Robert V. Townend, Bailey Townshend, Tykocinski Tykociner, Manuel S. Vallarta, Pierre Van Dyck, C. Wackmann, Lawrence Wainwright, Fred. W. Warburton, Jean J. Weigle, Joseph Wilczewski, Ralph E. Winger, Alfred Wolf, Wladimir M. Zaikowsky, Robert V. Zumstein, Vladimir K. Zworykin.

The regular scientific session consisted of 48 papers, abstracts of which are given on the following pages. Paper No. 9 was read by title. An **Authors Index** will be found at the end.

HAROLD W. WEBB, *Secretary.*

ABSTRACTS OF PAPERS

1. The K and L absorption and emission spectra of tungsten. CHARLES B. CROFUTT, University of Iowa.—Simultaneous photographic records of the absorption and emission spectra of the K and L series of tungsten were made on the same plates. This made it possible to determine the relative positions of the absorption edges and the emission lines under identical experimental conditions. The wave-lengths were measured and the results for the absorption edges are: K series 0.1780 A; L series 1.2122 A, 1.0716 A and 1.0217 A. In addition to the $K\beta_3$ line found by de Broglie, four new lines were found in the L series; β_{15} 1.2432 A, β_{16} 1.2166 A, γ_{12} 1.0748 A and (N) 1.9699 A. The $K\alpha_3$ line was not obtained. Of the new lines found β_{15} and β_{16} are in agreement with the selection principle and γ_{12} is given by a transition between two energy levels but not by the selection principle. The (N) line does not fit into any scheme. Attempts to identify it as an impurity failed. There are now four lines, β_{10}, β_9, γ_{12} and γ_{11}, agreeing with the energy level idea but not agreeing with the selection principle, and two additional lines β_8 and (N) not agreeing with either.

2. The temperature effect on the regular reflection of x-rays by aluminum foil. E. H. COLLINS, University of Iowa.—The intensity of the scattered x-radiation, wave-length .710 A, was measured at angles of 12° to 39° with the incident beam by an ionization chamber and an electrometer. The spectrometer used employs the principle of the powder method of crystal analysis. The scattering curves plotted from the observed data show peaks at 17.4°, 20°, 28.7°, and 33.8° due to the regular reflection of x-rays from the aluminum crystals. From the relative heights of these peaks the ratio of the intensity of scattered x-radiation at high temperatures to the intensity of the scattered x-radiation at low temperatures was observed and compared with the same ratio calculated from Debye's theory. It was found that the decrease in intensity of the regularly

reflected x-rays with increase in temperature was markedly greater than that predicted by theory. It was also found that this decrease was distinctly greater with increase of angle than is predicted by theory. The conclusion is reached that Debye's theory of the effect of temperature on the scattering of x-rays is inadequate. Since the intensity of radiation between the peaks was small and probably contained regularly reflected radiation of wave-lengths other than .710 A, no comparison with theory was made of the change of intensity of the general scattered x-radiation with change in temperature of the scattering material

3. A corpuscular quantum theory of the scattering of polarized x-rays. G. E. M. JAUNCEY, Washington University.—The method of a previous paper (Phys. Rev. **22,** 233, 1923) is applied to the case of the scattering of polarized x-rays. A formula is derived giving the intensity of the x-rays scattered in any direction when x-rays of any wave-length λ are scattered. In particular, the ratio of the intensity scattered in the direction of the electric vector of the primary beam to that scattered in a direction perpendicular to both the electric vector and the direction of the primary beam is found to be $(F^2/4)/(1+F/2)^2$, where $F=2\alpha$ or $2\alpha+\alpha^2$ (as in the previous paper) and $\alpha=h/mc\lambda$. This ratio is not zero as Thomson's theory requires. The scattered intensity becomes zero in the plane containing the electric vector and the primary beam for a scattering angle ϕ_p where $\cos\phi_p=F/(2+F)$. The angle ϕ_p may be called the polarizing angle. This angle is 90° for very long wave-length x-rays, but is about 80° for x-rays of wave-length 0.12 A.

4. On the theory of the refraction of x-rays. E. O. HULBURT, University of Iowa.—Accurate measurements by Stenström, Siegbahn, Hjalmar and others have shown that the wave-length of x-rays when determined by means of the Bragg formula $n\lambda=2d\sin\theta$, for the same line in different orders was not constant but decreased slightly with increase in order. C. G. Darwin suggested that the deviations from the Bragg relation might be attributed to the refraction of the x-rays in the crystal, and derived a formula whereby the refractive index may be determined from these deviations. The formula, however, gives values of $1-\mu$, μ being the refractive index, which vary from 10^{-4} to 10^{-6} for the same wave-length and crystal. This indicates that Darwin's suggestion may require modification. Assuming a refractive index of unity and making use of A. H. Compton's quantum theory of scattering of x-rays, it was found that deviations from the Bragg Law of about the right order of magnitude occur but of the wrong sign. With the assumptions (1) that the crystal possesses a refractive index differing from unity and (2) that the quantum scattering is operative, the values of $1-\mu$ again show large variation. It therefore appears probable that further modifications of the hypotheses are necessary, although more exact measurements of the x-ray wave-lengths are needed before a final conclusion can be reached.

5. On the photo-electric effect of Röntgen rays. JAKOB KUNZ, University of Illinois.—From the theory of the increase of the wave-length by the scattering of Röntgen rays given by A. H. Compton, it follows that the velocity of recoil of an electron is $v=(2h\nu/cm)\sin\theta/2$, where the angle θ varies from 0 to π. This law is very different from the law of the photo-electric effect of Röntgen rays given by the equation $\frac{1}{2}mv^2=h\nu$. The consequences of Compton's expression are pointed out, especially the necessity of using the relativity expression for the mass of the electron, if its velocity can not exceed that of light.

6. A law of periodic relationship of atomic radii. WHEELER P. DAVEY, Research Laboratory, General Electric Company.—Using the radii of the atoms of elements as determined by the "distance of closest approach" in crystals, the law is as follows: The ratio of the radii of any two elements on the left hand side of the same vertical column

of the Mendelejeff Table is approximately the same as the ratio of the radii of any other two elements on the same horizontal lines of the table provided that these elements also lie on the same side of a common vertical column. In the second horizontal row of the table, Mg and Si act in accordance with this law if they are placed on the left hand side of their respective columns instead of being given their usual positions.

7. Selection principle: A development based upon the Stokes-Thomson pulse theory. C. N. WALL, University of Illinois (Introduced by Jacob Kunz).—The selection principle due to Rubinowicz is deduced by elementary methods. Use is made of the Stokes-Thomson theory for the energy radiated by an accelerated electron. By working with a vibrational or equivalent elliptical orbit it is possible to set up a relation between the energy and the angular momentum radiated by an electron in passing around its equivalent orbit according to the classical theory. Upon applying the quantum theory to this relation the principle of selection may be deduced immediately.

8. Balmer lines from hydrogen in certain gases. E. O. HULBERT, University of Iowa.—Continuing experiments of a former paper (Phys. Rev. **22**, 24, 1923) the *Stark quantum broadening* of the Balmer lines of hydrogen mixed with carbon monoxide, with carbon dioxide, with air, and with oxygen, was found to be much the same as with the mixtures with nitrogen and with helium. Mercury vapor in the hydrogen discharge tube extinguished the hydrogen lines in favor of the mercury spectrum before any broadening was noticeable. As anticipated, the condensed discharge through water vapor gave the broadened Balmer lines just as through a mixture of hydrogen and oxygen. The condensed spark in air between aluminum electrodes wet with a small stream of water, showed the Balmer lines much broadened. The continuous spectrum from the spark under water and under certain alcohols may be looked upon as an extreme case of the Stark broadening of some or all of the aluminum, oxygen, hydrogen or carbon lines.

9. An extension of the Balmer absorption series of hydrogen. E. O. HULBURT, University of Iowa.—The light from a spark under water between phospor-bronze terminals was passed through a tube 80 cm in length filled with glowing hydrogen. The Balmer series appeared as narrow dark absorption lines against the continuous spectrum from the spark. The series was traced to the tenth Balmer line, taking $H\alpha$ to be the first. This is an extension of eight lines over previous laboratory results.

10. The secondary spectrum of hydrogen. O. S. DUFFENDACK, University of Michigan.—The excitation of the secondary spectrum of hydrogen by electron impacts below the ionization potential was investigated by two methods: (1) by a low voltage arc in a mixture of hydrogen and mercury vapor, and (2) by hydrogen alone excited in a three-element tube having a gauze very close to the filament so as to obtain a large thermionic current without striking an arc. *In the mixture*, the Fulcher bands and other strong lines, notably groups at $\lambda 4625-4634$ and $\lambda 4562-4580$, appear at 13 volts and increase rapidly with the voltage. Nearly the whole secondary spectrum is present at 14 volts. $H\alpha$ appears at 11 volts with no trace of $H\beta$ until 12 volts. These values are slightly less than their radiation potentials given by Bohr's theory, probably on account of the initial velocity of emission of the electrons. *The three electrode tube* gave similar results except that the potentials were one volt higher, the spectrum being practically complete at 15 volts. Only faint traces of the Balmer lines was seen below 16.5 volts. The appearance of these lines in the mercury mixture is accounted for by the dissociation of hydrogen by impacts with excited mercury atoms.

11. Notes on the theory of the fine structure of H and He^+ lines. L. B. HAM, University of Illinois.—The method of Glitscher (Ann. der Phys. **52**, 608, 1917) was used on the equations $E_k=\frac{1}{2}mv^2$; $m=m_0(1-\beta^2)^{-\frac{1}{2}}$. The resulting energy equation gave a

value for the hydrogen doublet of the Balmer series twice that given by relativity. A similar calculation for the L-doublets of the Röntgen spectra gave results not compatible with experiments. The electromagnetic emission theory of J. Kunz (Phys. Rev., **3**, 464, 1914) gives the same results as relativity. The mass variation of the electron in jumping from orbit to orbit has been considered by two principles (1) $dm=dE/c^2$; $m=m_0(1-\beta^2)^{-\frac{1}{2}}$. There is a close agreement found between the two values of dm but the signs are different. This study has been extended to elliptic orbits.

12. Life of metastable helium. FABIAN M. KANNENSTINE, University of Chicago. —The critical 4.8 volt striking frequency for alternating helium arcs was obtained under improved experimental conditions. The critical frequency decreased rapidly from 260 cycles per second at 0.15 mm pressure to 120 cycles at 0.75 mm, more slowly to 70 cycles at 2mm, and remained practically constant at 70 cycles to 10mm. The critical frequency increased very slightly as the arc length decreased from 30 mm to 10 mm for pressures below 3.5 mm, but was practically independent of the arc lengths used for pressures above 3.5 mm up to 10 mm. The constancy of the critical frequency over a large range of pressures and arc lengths is more naturally interpreted on the conception of a long lived abnormal atom, than on ideas which suggest a strong dependence on pressure, such as the handing on of radiation or the imprisonment of radiation as suggested by F. Horton and Ann C. Davies, and by K. T. Compton. The departure from constancy at low pressures may be interpreted as due to such rapid diffusion of abnormal atoms from the arc space that higher frequencies are necessary to obtain an indication of striking.

13. Evidence of a spark line in the lithium spectrum. F. L. MOHLER, Bureau of Standards.—The spectrum of a thermionic discharge in lithium vapor was photographed at potentials ranging from 8 to 200 volts. The only noticeable change in the spectrum was the appearance near 50 volts of a line at λ 2934.15 I. A. The line was barely visible at 45 volts, strongly enhanced above 55 volts, and reached nearly full intensity at 100 volts. At this potential the photographic density was about that of the sixth line of the principal series. This indicates a critical potential for the K limit of about 50 volts, which falls within the range of the rather discordant results of other methods of measurement. The observed line may correspond to the helium doublet λλ10829, 10830.

14. New members in the series spectrum of trebly-ionized silicon. R. A. SAWYER, University of Michigan and R. F. PATON, University of Illinois.—The series spectrum of trebly-ionized silicon has recently been published by A. Fowler (Proc. Roy. Soc. **A103**, 413, 1923), and that of doubly-ionized aluminum by F. Paschen (Ann. der Phys. **71**, 142, 1923). These two spectra are closely related, as is to be expected from Kossel and Sommerfeld's displacement law. The spectrum of silicon, however, has not been so completely worked out as that of aluminum. This is partly because the spectrum of trebly-ionized silicon lies farther in the ultra-violet than that of doubly-ionized aluminum so that many of the higher members of the silicon series are out of reach. Some of the missing members of the silicon series however are in the ordinary photographic region. The authors (Astrophys. J. **57**, 279, 1923) have recently made a study of the vacuum spark spectrum of silicon in the course of which many new lines have been measured. The list of new silicon lines has been inspected for possible coincidences with previously missing members of the silicon series. The following series members are apparently present among the new silicon lines: $5\pi_1-6\sigma$; $5\pi_2-6\sigma$, $5\pi_1-7\sigma$, $5\pi_2-5\delta$, $5\pi_1-6\delta$, $5\pi_2-6\delta$, $4\phi-5\delta$, $5\phi'-7\phi''$. The line $5\pi_2-7\sigma$ is obscured by an aluminum impurity. The terms are expressed in the new Bohr numeration.

15. The ultra-violet absorption spectra of the spark in water between metallic electrodes. E. O. HULBURT, University of Iowa.—Experiments by Hale, Finger and others have shown that the spectrum of the spark under water between metallic elec-

trodes exhibits a continuous spectrum crossed by bright and dark lines characteristic of the metal. The present work is a further study of this phenomenon. Spectrograms with dispersion 8 A. U. per mm have been taken in the region λ 4400 to λ2400 A of the under-water spark produced by the discharge of a 0.007 microfarad condenser connected to a 25 kv transformer. Absorption lines were obtained from aluminum, antimony, bismuth, cadmium, chromium, cobalt, copper, iron, lead, magnesium, molybdenum, nickel, silver, tin, and zinc. Certain emission lines also appeared. In the case of gold, platinum, iridium, and tungsten the emission lines were numerous, but the absorption lines were few and were so near the short wave-length end of the plate where the spectrum faded out that their origin was somewhat doubtful. A detailed study of the plates and an attempt to extend the observations further into the ultra-violet is in progress.

16. Low voltage spectrum of mercury. JOHN A. ELDRIDGE, University of Wisconsin.—According to the Bohr theory the lines of the arc spectrum should appear before ionization, appearing in successive groups as the voltage is raised. For the metals of the first column of the periodic table one, and in the second column two such low voltage lines are recognized. The non-appearance of the complete arc spectrum in spectrograms taken below ionization is due to space charge; the only effect of ionization upon the spectrum is probably the elimination of this space charge. The impressed voltage can be maintained before ionization only in the immediate proximity of the electrodes, and it is here that the low voltage spectrum is observed. Spectrograms of mercury show the lines appearing below ionization group by group at voltages agreeing with the theoretical values.

17. Dissociation of hydrogen and nitrogen by mercury atoms excited in an arc. K. T. COMPTON, Princeton University and O. S. DUFFENDACK, University of Michigan. —Arc at various voltages, with and without the admixture of mercury vapor, were maintained between a hot molybdenum cathode and a nickel anode in hydrogen and nitrogen. Suitable agents were present to absorb atoms of these gases, when they were produced by dissociation of molecules, and the rate of dissociation was taken as proportional to the rate of decrease of gas pressure. *Dissociation of hydrogen.* Hydrogen in an electric arc discharge disappears, presumably by dissociation and subsequent chemical action, at an abnormally rapid rate under conditions in which excited mercury atoms are present in large concentration. This is interpreted as due to transfer of the energy of the excited mercury atoms to hydrogen molecules at collisions, dissociation being thereby effected. *Dissociation of nitrogen.* Nitrogen is caused to disappear from a tube by electronic bombardment at voltages above the ionizing potential but at a considerably less rate than hydrogen. The presence of excited mercury atoms causes a much smaller increase in the rate of disappearance of nitrogen than of hydrogen, and is probably due to the action of atoms having an electron displaced to the $2P$ orbit.

18. The mechanism of the positive column of the mercury arc. IRVING LANGMUIR, Research Laboratory, General Electric Co.—The volt-ampere characteristic of an electrode, preferably spherical in shape, in a mercury arc is used to measure the electron and positive ion current densities, and the distribution of electron velocities. The electrode is automatically screened from the ionized gas by the space charge in a positive ion or electron sheath (thickness about 0.1 mm). The glass wall of the tube is 10 to 15 volts negative to the ionized gas and collects all positive ions moving towards it, but reflects elastically 99.8 per cent of the electrons, which lose not over 0.5 per cent of their energy by reflection. The tendency of the gas to move toward the anode results from the inelastic collisions of the ions against the wall and is not evidence of negative ions. The electron velocities have Maxwellian distribution; the average energies of the electrons correspond to 3.9 volts at 1.0 bar and 1.7 volts at 33.0 bars mercury vapor pressure, and are independent of the arc current. Ordinary sounding electrodes in

ionized gases are wholy condemned as they cause errors of 5 to 40 volts. The anode drop usually does not exceed 2 to 3 volts and may often even be negative.

19. The distribution of luminosity throughout a potential cycle for a neon glow discharge lamp. ENOCH KARRER and A. PORITSKY, Nela Research Laboratories.—The relative intensity of the light emitted by a neon glow lamp as a function of time may be represented by some exponential curve which is somewhat asymmetrical with respect to the maximum, being slightly more abrupt on ascent than on descent. When relative illumination is plotted against current there appears to be some hysteresis. The method of obtaining these data was by the use of an oscillograph. The observing drum, driven by a 60 cycle synchronous motor, was illuminated through a slit by the neon glow lamp. When the drum rotates in synchronism with the exciting potential two stationary luminous streaks appear whose brightness may be measured at any desired point. Since the brightness is low a special photometer wss designed. The position of the photometer as it is moved across the streaks may be correlated with the period of the alternating potential by observations on the voltage and amperage records formed upon the drum in the usual way.

20. Interference bands produced by mica and the use of mica windows in infra-red spectroscopy. CHARLES F. MEYER and DETLEV W. BRONK, University of Michigan.—When light from an incandescent source is *reflected* by a thin sheet of mica into an ordinary spectroscope, the spectrum is seen to be crossed vertically by regularly spaced dark bands, caused by the interference of light reflected from the front and rear surfaces. For *transmitted* light there should be corresponding variations of intensity through the spectrum. Variations in the intensity in the infra-red spectrum, found some years ago, were ascribed to interference in the mica forming the windows of the absorption cells containing gases, but no special study was made of their cause. In some recent work large variations in the intensity were found which might have caused serious errors in absorption measurements. The interference has been studied and a method of overcoming the variations in intensity found. Graphs are shown for the variations in ntensity for a cell with four windows, of the variation caused by a single sheet of mica placed normal and at small angles to the beam, for mica rotated through a large angle (30°), in which case the variations are eliminated, and for a cell having four windows all at 30°.

21. A new method of utilizing polarized light in crystallographic analysis. L. W. TAYLOR, University of Chicago.—The petrographic microscope is not readily applicable to the examination of opaque specimens. Since the characteristics of reflected polarized light depend upon the angle of incidence, the instrument used must be focused for parallel light. A microscope must therefore be replaced by a telescope. A goniometer has been fitted with a combination of polarized light accessories. With this both the usual crystal measurements and the polarized light observations have been made with one setting of the crystal.

22. On the isolation of the initial and final positive air ions. HENRY A. ERIKSON, University of Minnesota.—At an earlier meeting (Phys. Rev. **17,** 400; **18,** 100, 1921; **20,** 117, 1922) the writer reported the existence in air of an initial positive ion, which changes in about 0.1 sec. on the average, into the final positive ion which has a mobility of 1.36 *cm/sec/volt/cm.* In the earlier measurements it was possible to determine only the initial and final states of the ions, as the apparatus used did not have sufficient resolving power to isolate the two when present in the air at the same time. By increasing the air velocity to 2000 *cm/sec* and also the potential at right angles to the air current, correspondingly, it has been found possible, beginning with air in which both ions were present, to isolate the two. The degree of isolation is represented by a 50 per cent

depression in the positive curve between the maximum for the initial ion and that for the final ion. No trace of separation has been obtained in the case of the negative ion.

23. Impact ionization by low speed positive ions. M. A. TUVE, University of Minnesota (Introduced by John T. Tate).—*Mercury ions in mercury vapor; delta-ray effect at low velocities.* Positive ions produced by electronic collision in mercury vapor were accelerated through potentials of 25 to 240 volts into an ionization chamber where they collided with mercury atoms. With vapor pressure adjusted to give a calculated molecular mean free path of one fourth the length of the chamber, the electron current in the chamber was measured. To evaluate the photo-electric effect, the current was again measured under identical conditions of primary ionization but with potentials adjusted to prevent positive ions or delta-rays from entering the chamber. The ratio of the difference between these two electron currents to the total positive ion current in the most reliable set of data was 1/7300 at 25 volts, 1/5600 at 115 volts, and 1/4500 at 240 volts maximum velocity of the ions. If no delta-rays are emitted these ratios give a measure of the amount of impact ionization by the positive ions. In any case they give definite *upper limits* to the amount of this ionization. The variation of the ratios with pressure indicates that the delta-ray effect was large and that there was probably no impact ionization at these potentials. The ratio at 240 volts *increased* to 1/300 when the pressure was reduced to 1/20 of its former value, a condition in which impact ionization was very improbable. Similar work is in progress with hydrogen.

24. The ionizing efficiency of electrons at different energies of impact. A. LL. HUGHES and ELIAS KLEIN, Nela Research Laboratory.—Electrons were accelerated from an incandescent tungsten wire to a plane perforated plate, through which a small fraction passed and experienced in the space between the perforated plate and a parallel plate a retarding field of sufficient magnitude to prevent any reaching the latter plate. The arrangement is practically the well known Lenard scheme for investigating ionizing potentials. The positive ions formed in the region between the plates were driven to the unperforated plate, and the positive ion current was measured per unit electron current passing into the space as a function of the voltage of the perforated plate. A formula was derived giving the fraction of collisions $f(V')$ resulting in ionization, at any energy of impact V', in terms of the potential of the perforated plate, the distance apart of the plates, the pressure, and the mean free path. For all gases, $f(V')$ rose very rapidly from the ionizing potential to a maximum, after which there was a pronounced, though less rapid, decrease. The positions of the maxima are at 147, 162, 80, 74, 101, and 80 volts for helium, neon, argon, hydrogen, nitrogen, and metane respectively. The values of the function $f(V')$ at the respective maxima are .11, .14, .35, .21, .27, and .32. Thus, even under the most favorable conditions of impact, the majority of collisions are non-ionizing.

25. On the relative ionization in different gases for slow-moving electrons. WILLIAM P. JESSE, Yale University.—A beam of electrons of almost uniform velocity, corresponding to a p.d. of approximately 200 volts was passed through different gases at low pressures. A sensitive galvanometer measured the number of positive ions formed in each case for a constant electron current. The pressure was varied from 10^{-5} to 10^{-3} mm, as measured on a McLeod gauge, and a straight line relation was obtained for each gas between the pressure and the positive ion current. A comparison of the slopes of these lines gave the relative ionization in the various gases. For the gases studied—helium, hydrogen, methane, carbon monoxide, argon and neon—the relative ionization was not found, in general, to be proportional to the atomic number, or sum of atomic numbers, of the individual molecules. With neon as a standard, the relative ionization was as follows: neon 1, helium 0.487, carbon monoxide 3.44, hydrogen 0.91, methane 3.45, argon 4.33. The ratio between the values for hydrogen and helium is in fair agreement with the ratio derived from the theoretical formula of J. J. Thomson.

26. Determination of the mobility of the ions in the corona discharge. WM. M. YOUNG, University of Illinois (Introduced by Jakob Kunz).—To test the theory of the corona pressure given by Jakob Kunz, the mobility of the ions in the corona discharge has been directly measured by blowing the gas first through the corona and then into two cylindrical potential chambers, the first neutralizing a certain number of charged ions, the second (a measuring chamber) determining the charge on the remaining ions. The ionization current in this second chamber shows well defined maxima which depend upon the potential difference. The mobility of the ions of the gases measured, CO_2, N_2, and O_2, agree very well with those deduced by Kunz from the pressure increase alone.

27. The paths of electrons in the magnetron. ALBERT W. HULL, Research Laboratory, General Electric Company.—A special solution of the magnetron equations has been found for magnetic fields stronger than the critical value, in which all the electrons move in concentric circles around the cathode. This system of circular orbits gives a total space-charge three times as great as the quasi-cardioid orbits previously considered (Phys. Rev. **18**, 31, 1921) and the forces exerted at collisions between electrons are such as to gradually change the cardioid orbits, if they existed, into circular orbits. That the circular orbit system is the one which actually exists is evidenced by measurements of the positive ionization, which increases suddenly exactly three-fold, in agreement with theory, when the critical magnetic field is reached. The electron distribution in this rotating beam of electrons is unique. The electron density is constant throughout the beam, and the velocity of rotation is proportional to the distance from the center. Hence the electrons in the beam maintain their relative positions giving a solid shaft of rotating electricity composed of a space-lattice of equidistant electrons.

28. The trace left by a helical beam of electrons on a plane perpendicular to its axis. C. J. LAPP, University of Iowa.—If electrons with a distributed velocity projected from a point source are caught in a magnetic field making an angle ϕ with the line of projection, a spiral will be formed. If a photographic plate is placed in the path perpendicular to the axes of the spiral a trace will be left on the plate. The equation for this trace when written in polar coordinates has been found to be of the form

$$\rho = (K \sin \pi\lambda)/\pi\lambda$$

where K is a constant involving such terms as mass and charge of the electron and strength of the magnetic field, and λ varies from zero to infinity. The equation when corrected for the change of mass of the electron with velocity is quite involved. This has been plotted and shown to be like the actual traces left on a photographic plate.

29. Reflection of electrons caused by light. IRVING LANGMUIR, Research Laboratory, General Electric Co.—When white light falls on a nickel electrode in caesium vapor at low pressure the surface becomes activated so that it is capable of reflecting electrons which strike it. As the number of electrons that can be reflected is strictly proportional to the light intensity it appears that in the act of causing the reflection, adsorbed caesium atoms are deactivated. Under given conditions the number of electrons reflected from one electrode and collected by another increases at first proportionally to the light intensity, but reaches a limit so that the photo-reflection current becomes independent of the light intensity, although it then varies with the primary electron current, the caesium vapor pressure, the voltages on the electrodes or an applied magnetic field. In the region where it is proportional to the light it is independent of these factors. This photo-reflection is absent with red light and is due mainly to light of wave-length about 5300 A. Normal photo-electric currents from the same electrode are produced by visible light of any color, but with white light the normal photo-current is only about 1/200 of the photo-reflection current.

30. Electron emission from caesium-covered filaments. K. H. KINGDON AND IRVING LANGMUIR, Research Laboratory, General Electric Company.—As reported

before (Phys. Rev. **21**, 380, 1923), caesium vapor forms a strongly adsorbed monatomic film of Cs on a clean tungsten filament. If the bulb contains Cs at a temperature of 30°C, the maximum electron emission from the Cs film on the filament is about 88×10^{-6} amp. per cm², and occurs at a filament temperature of 690°K. An increase in the pressure of Cs vapor enables the adsorbed film to be maintained at higher filament temperatures, and the maximum emission increases about in proportion to the Cs pressure. Contamination of the filament surface by a trace of residual gas in the tube (such as CO) increases the maximum emission considerably. The increase in emission is particularly conspicuous if a monatomic adsorbed film of oxygen is formed on the filament before admitting the Cs. The oxygen layer sticks to the tungsten up to about 1600°K, and acts as a binder for holding Cs on the filament surface. With a bulb temperature of 30°C the maximum emission from the Cs film is now about 350×10^{-3} amp. per cm², and occurs at a filament temperature of 1000°K. An electron emission of 0.38 amp. may be obtained by the expenditure of 1 watt in the filament. Similar effects are obtained by treating Mo or Th surfaces with oxygen and Cs.

31. A note on the thermodynamics of thermionic emission. C. DAVISSON, Research Laboratories of the American Telephone and Telegraph Co. and the Western Electric Co., Inc.—The thermodynamic argument which leads to the thermionic relation $\log_e i=\log_e(AT^{\frac{1}{2}})+\int(\omega/KT^2)dT$ is based upon a consideration of the reversible changes that may be carried out in a system comprising a hot body in equilibrium in an enclosure with an atmosphere of electrons. In order to simplify the argument it is customary to assume that the number of gaseous electrons is so small that the electrostatic field to which they give rise is negligible. Subject to this limitation the volume density of such electrons is then regarded as uniform and the argument is carried through as in the case of an ordinary vapor in equilibrium with a condensed phase. This puts a superior limit upon the temperature of the system and strictly speaking imposes the same temperature limit on the validity of the conclusions that may be drawn from the argument. This limitation may be removed by treating a system of simple geometry taking into account the actual distribution of the gaseous electrons subject to the conditions $\nabla^2\phi=4\pi\rho$ and $\log\rho-\phi e/kT=$constant, and including in the intrinsic energy of the system that represented by the electrostatic field. This more rigorous argument leads to the same conclusion as the simple one.

32. Electronic bombardment of copper. H. E. FARNSWORTH, National Research Fellow, University of Wisconsin.—The secondary electron characteristics of copper, for low primary velocities, have been investigated in detail, after the copper had been thoroughly outgassed at a temperature as near the melting point as possible. Measurements of the velocity distribution of the secondary electrons indicate that inelastic collisions of the primary electrons occur at voltages corresponding to the resonance and ionization potentials of copper, 3.8 and 7.7 volts, respectively, computed from spectroscopic data by means of the quantum relation. The curve obtained by plotting the ratio of the secondary to the primary current as a function of the accelerating primary voltage also shows changes in slope which check with these values. These results strongly indicate that the resonance and ionization potentials of a metal may be obtained by this method of electronic bombardment.

33. Standard cell construction. A. C. Longden, Knox College.—A discussion is given of the relative merits of the Clark and Weston cells, and of the defects in the Clark cell and of suggested methods of eliminating them. The questions of lower temperature coefficient, higher e.m.f., longer life, and simpler construction are treated. New forms are described in which the platinum-glass joint in the amalgam limb will not crack. Records of a group of cells are given.

34. Dielectric fatigue in Rochelle salt. JOSEPH VALASEK, University of Minnesota.—The dielectric constant of Rochelle salt determined at 0°C by means of a ballistic galvanometer is apparently 800 for the ordinary charge, while for a discharging time of 0.03 sec. it is 720, and for a frequency of two million cycles it is, according J. G. Frayne, about 80. This indicates that either conduction or residual charge accounts for the greater part of the low frequency values. The behavior of the substance is as though it contained conducting elements insulated from one another. While ordinary residual charge increases the discharge when the time of charging is increased, an oppositely acting "fatigue" effect decreases the discharge by as much as 100 per cent when 100 volts are applied for ten hours. The discharges for the opposite direction of charging are simultaneously increased. These effects diminish with time in an approximately exponential manner when the charging potential is removed. The variation of the dielectric displacement with the field is not linear for either low or high frequencies, and fatigue causes it to follow a hysteresis loop. One finds that the fatigue is due to a subtraction from the effective externally applied field of a semi-permanent internal field which is produced either by a very slow polarization or by a space charge created by internal conduction. These anomalous effects have been observed only between—20°C and + 25°C, the range in which the crystal is piezo-electrically active. There is a corresponding piezo-electric fatigue due to the same causes.

35. The threshold current carried by a supraconducting wire. G. Breit, University of Minnesota.—Silsbee (J. Wash. Acad. 6, 597, 1916) advanced an explanation of the phenomenon of threshold current as a consequence of the threshold magnetic field which was modified and corrected by Langevin. In the modified solution (Silsbee, Bur. Stds. Sci. Pap. No. 307) a transition layer is introduced in which the current density has values intermediate between those corresponding to the ordinary and the "supra" values. One might question the physical validity of this picture. The difficulty is removed by introducing intermediate values of conductivity. Taking the dependence of conductivity on field to be linear the writer convinced himself that Langevin's solution is approached as a limit when the transition range of the field becomes infinitesimal.

36. On the resistance of thin metallic films and foils when exposed to x-rays. R. A. ROGERS, University of Iowa (introduced by C. J. Lapp).—An attempt was made to determine if the resistance of thin metallic films and foils could be changed by exposure to x-rays. Thin films of Bi, Cu, Pd, and Ni, prepared by the methods of cathodic disintegration and evaporation, and thin foils of Au and Al, varying in resistance from 10 to 3000 ohms, were placed in a broad beam of x-rays. Their resistance was measured by means of a very sensitive extended-arm type of Wheatstone bridge which had been accurately calibrated to measure changes of resistance as small as one part in one million. Certain spurious effects were found and eliminated. No change of resistance could be detected.

37. The effects of tension and magnetization upon the electrical resistivity of permalloy. H. D. ARNOLD and L. W. MCKEEHAN, Research Laboratories of the American Telephone and Telegraph Co. and the Western Electric Co., Inc.—The experiments here discussed, forming part of a more extended study of permalloy, were made upon wires and tapes of a nickel-iron alloy containing approximately 78.5 per cent nickel and 21.5 per cent iron. Straight samples were examined in conditions resulting from various preliminary treatments, including those which made the initial permeability much greater than that of hitherto available magnetic materials. It appears that the maximum increase in electrical resistance, of the order of two per cent, is the same whether produced by tension or by magnetization, but that characteristic differences in the initial stages of the two effects point to fundamental differences in the directness of control of resistivity by mechanical and by magnetic means.

38. Some experiments on magnetic rotation in sputtered cobalt films. L. R. INGERSOLL, University of Wisconsin.—Cathodically deposited films of cobalt show, in general, a decrease of magnetic rotation with increasing wave-length out as far as they can be tested by the writer's method (2.2μ). However, when heated in low pressure hydrogen to 300°C for a number of hours the form of the curve is reversed and the rotation is greater for longer wave-length, while in some cases for a certain wave-length in the visible it is practically unchanged. Assuming that heat treatment results in a coalescing of the granules of metal, these experiments indicate that magnetic rotation in such films is dependent on the size and state of aggregation of the particles and is therefore a *molar* rather than a *molecular* phenomenon. Results of magnetic rotation measurements on colloidal iron in isobutyl alcohol support this view, for these show no effect above that of the pure alcohol. While clearly magnetic in character the particles of iron are apparently too small to cause appreciable magnetic rotation.

39. The problem of gas degeneration. WORTH H. RODEBUSH, University of Illinois.—In the formula for the entropy of a monatomic gas the quantum is introduced by assuming the generalized space to be divided into cells whose faces have the area h. h is of the dimensions, momentum $\times$ length, and if we knew the average length $\bar{l}$ for these cells we could calculate the average quantum of momentum for the gas. Assuming $\bar{l}=K_0(V/N)^{1/3}$ then $mV=nh/K(V/N)^{1/3}$, and the distribution law becomes $N_n=K_1e^{-n^2\epsilon_0/kT}$ where $\epsilon_0=Kh^2/2m(V/N)^{2/3}$. From the distribution law, C_v and the integral from 0 to T of $C_v d(\log T)$ can be obtained. From these it appears that the entropy of an ideal gas at 0°K differs from zero, if at all, only by a dimensionless constant. C_v shows irregularities analogous to those of the rotational specific heat curve. If account were taken of all the possible quanta in a gas instead of assuming an average quantum, a more regular curve would be obtained for C_v and deviations from $3R/2$ would appear about where Eucken found them for helium.

40. An experimental study of the relation of the density of a gas to pitch. CHAS. T. KNIPP and W. B. WORSHAM, University of Illinois.—The *new singing tube* was used in this study. By Laplace's theory of sound propagation the velocity v of a sound wave is given by the expression $v=N4l=\sqrt{\kappa RT}$ where N is the frequency, l the length of the vibrating column, t the constant 1.41 R the gas constant, and T the absolute temperature. By observing two gases, using the same tube, we at once get $N_1/N_2=\sqrt{R_1/R_2}=\sqrt{\delta_2/\delta_1}$, where δ is density. The standard gas (in this case air) and thegas under observation were introduced in turn into the singing tube through a samll mercury valve. The frequencies were read off on a standard tone variator. The following table shows the results for a few of the gases tested.

Gas	Density	N (calc.)	N (obs.)
air	1.0000	195	195
ammonia (NH_3)	.5962	253	252
carbon dioxide (CO_2)	1.5290	160	162
hydrogen (H_2)	.0695	740	738
chlorine (Cl_2)	2.4900	124	125

41. Acoustic wave filters in series. G. W. STEWART, University of Iowa.—Earlier reports by the author show that low-frequency-pass and single-band filters not only give very small attenuation in the regions computed by a simple theory, but also produce transmission bands at higher frequencies, the location of which can be ascertained by an extension to the theory. These facts arouse interest as to what might be accomplished by placing acoustic wave filters in series. The following are the results of present experiments: (1) It is possible to construct a low-frequency-pass filter without additional and undesired transmission bands, by placing two previously computed low-frequency-pass filters in series. (2) By the series arrangement of a low-frequency-pass

and a single-band filter or of two single-band filters, it is possible to construct a single-band filter without the additional transmission bands. (3) The reflections occurring at the junctions of such filters do not seem to influence the results adversely. Indeed the transmission in the selected region is usually greater than could be expected from the action of the filters separately. This is in accord with observations on the effect of end reflections at cut-off frequencies.

42. Acoustic wave filters in solid and liquid media. V. C. HALL, University of Iowa.—The theory of acoustic wave filters previously developed (Stewart, Phys. Rev. **20,** 528, 1922) is based upon assumptions that apply only to fluids. It was thought, however, that such filtering action in solids might be experimentally determined. Filters were built of brass, the main channel being a brass rod, 40 cm long and 4 mm in diameter, with two branches 20 cm apart. Branches were made of solid brass, either roughly spherical or in the form of plates, and fitted on the rod by means of a tapered brass collar. A high attenuation was found for all frequencies above a certain point for each of the eleven filters built, the frequency of cut-off varying from 1200 to 2200 d.v. per sec. No return of transmission was found although tests were made up to 9000 d.v. The cut-off frequency was found to vary as the inverse square root of the volume of the branch, as in the case of the acoustic wave filters in air. This leads to the conclusion that dilatational waves are far more important than distortional, and that there is a possibility of obtaining an approximate theory for the action of the filters in solids. Liquid filters were experimented with by filling an ordinary low-frequency-pass filter with water. The results agree with theory in that the frequency of cut-off varies as the velocity of sound in the medium.

43. Experiments with the pin-hole resonator. PAUL E. SABINE, Riverbank laboratories.—Barus discovered that if one arm of a sensitive manometer be connected by a minute funnel-shaped opening, a pin-hole, to the inside of a vibrating air column, the manometer will record a static pressure difference when the pin-hole is at a pressure loop of the stationary wave. Attempts have been made to utilize this phenomenon to determine the alternating pressure distribution in the standing wave system in a large rectangular empty room. The pin-hole was mounted in a movable piston, forming the closed end of a cylindrical resonator. The static pressure difference was measured by a tilted alcohol gage. It was found that the easily measurable pressure difference produced depended both in sign and in magnitude upon a large number of factors. Measurements showing the effects of the diameter of the pin-hole, the tuning of the resonator, changes in the acoustic conditions in the room under constant conditions at the source and resonator, and changes in the position of the source and the resonator under constant external condition, have been made. The results are too complicated to be briefly abstracted. The conclusion so far reached is that the action is associated with the vortex motions accompanying vibrations of large amplitude in a viscous medium. Further, the organ pipe source, the resonator, and the room itself constitute a coupled system, the elements of which mutually react upon each other in a way too involved to permit of analysis by this method.

44. Some characteristics of a hot wire sound detector. ORIN TUGMAN, Riverbank Laboratories.—A strip of platinum foil is mounted parallel to a slit, in a horizontal plane, over a chamber lined with hair felt, in an attempt to make a sound detector non-resonant. The resistance of the hot wire, measured by a potentiometer, is increased by sound when the wire is below the slit. If the strip is in the plane of the slit or above it, the resistance is decreased by sound. A manometer, attached to the apparatus, shows an increased pressure in the chamber, due to sound, when the strip is hot. This indicates that sound pulses pass more readily through the slit in a direction opposite to the air convection current than with it. The platinum strip is heated by the reduction

of the air convection from the hot wire when it is below the slit and is cooled by the blast of sound pulses through the slit, when the wire is in the slit or above it.

45. On a continuously tunable hydrophone. LOUIS V. KING, McGill University. —Diaphragms form an essential part of submarine sound receivers and generators. It is well known that a sound generator will radiate very little energy unless the frequency of the alternating force causing the diaphragm to vibrate is very close to the free period of the diaphragm. The same remarks apply to the receptive properties of submarine sound receivers, the best conditions for audibility being when the diaphragm is tuned to the frequency of the incident waves. The hydrophone described in the present paper is fitted with a specially shaped diaphragm of non-corrosive steel kindly furnished by Dr. Burgess of the Bureau of Standards. By altering the air pressure on the diaphragm from zero to 55 cm mercury, the natural frequency in air may be varied from 480 to 720 without overstressing. A series of resonance-curves in air, obtained by plotting amplitude of vibration against pressure for a series of fixed frequencies 24 cycles apart, show that sharpness of tuning in this hydrophone by air pressure is about as good as obtains in a good radio-telegraph apparatus by "tuning in" with a variable condenser. In the range of frequencies 480–720 it is possible to "tune in" to one of ten frequencies, others more than 24 cycles apart being eliminated sufficiently well to make signal reading by ear quite distinct. The hydrophone described is intended to form part of ship-board equipment allowing combined submarine and wireless signals to be received from a lighthouse in such a way that ships in fog may determine distance and bearing once a minute.

46. Binaural vs. monaural sensibility of the human ear to small differences in frequency. ROSCOE CONKLING YOUNG, University of Chicago.—*Tests with wide ranges of loudness and frequency.* A telephone receiver actuated by energy from a vacuum tube oscillator is used as a source of sound. The lower of the two notes used is produced by adding periodically a small variable capacity ΔC to the capacity of the oscillating circuit. Intensity is varied by a change in resistance. Tests made on ten persons of normal hearing at a pitch of 1,600 d.v. at current amplitudes from 4 to 4,906 times the threshold show that the barely perceptible percentage change in pitch, $100\ \Delta N/N$, is practically the same for the right and left ears, but is appreciably smaller for the two ears. Tests made on forty persons of normal hearing at pitches from 64 d.v. to 4,9066 d.v. at amplitudes 100 times the threshold show that $100\ \Delta N/N$ is essentially the same for each single ear, but lower for the two ears. Tests made on ten persons of normal hearing at pitches from 4,000 d.v. to 8,000 d. v. for amplitudes 100 times the threshold show a similar difference between one and two ears. Curves of other investigators are given for comparison.

47. Some further experiments on the pitch of musical tones. HARVEY FLETCHER, Research Laboratories of the American Telephone and Telegraph Co. and the Western Electric Co., Inc.—At the Washington meeting it was shown that the fundamental and a large number of overtones of a musical tone could be eliminated without changing the pitch. Further experiments have veen made using ten vacuum tube oscillators giving the frequencies 100, 200, 300, . . . , 1000 cycles per second as sources of sound. When these frequencies actuated a telephone receiver, a full musical tone of a definite pitch corresponding to 100 cycles was given out. Any three or more consecutive frequencies of the series was sufficient to produce a musical tone of this same pitch. When only two adjacent frequencies were used, they were heard as separate tones although the difference tone was plainly audible. As would be expected the combination 200, 400, 600, 800 and 1000 cycles gave a full musical tone of pitch 200. Such combinations as 100, 300, 500 and 700, or 100, 400, 700 and 1000 gave sounds which were not musical and which had no definite pitch. To make a combination of pure tones sound like a

single musical tone of definite pitch, it is necessary that the frequencies of the components have a common difference which is also a common factor of each component. The pitch of such a combination corresponds to the common difference frequency. These results can be explained from the mechanism of hearing and agree well with quantitative measurements of the response characteristics of the ear.

48. A quantum theory of uniform rectilinear motion. ARTHUR H. COMPTON, University of Chicago.—For uniform rectilinear motion, the quantum postulate $\int p\ dq = nh$ states that the momentum of a system is $p = nh/q_1$, where $q_1 = \int dq$ is the displacement required to bring the system back to its initial condition. The fact that a thing in uniform rectilinear motion repeats its initial condition at regular space intervals makes it in the general sense a train of waves, for which $\lambda = q_1$. Using Bohr's correspondence principle, each value of n is identified with the order of a harmonic component of the wave. For the nth harmonic, $\lambda_n = q_1/n$. Thus in general, for sine wave, $p = h/\lambda$. But the momentum of a wave-train of energy E and velocity v is $p = E/v$. Thus $E = hv/\lambda = hv$. The application of these equations to electromagnetic radiation is confirmed by the change of wave-length of x-rays when scattered and by the photo-electric effect. Thus also on the quantum theory radiation consists of trains of waves. Considering a moving diffraction grating of grating space D as a train of waves, its momentum is similarly nD/h, which is the basic hypotheses of Duane's quantum theory of diffraction.

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